CHEMICAL ANALYSIS.

PART I. QUALITATIVE.

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A MANUAL

OF

CHEMICAL ANALYSIS,

QUALITATIVE AND QUANTITATIVE.

FOR THE USE OF STUDENTS.

PART I.

QUALITATIVE.

BY

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CHAPTER I.

GENERAL REMARKS ON CHEMICAL ANALYSIS.

1. Chemistry is essentially an experimental science. Its object is the investigation of the material constituents of the globe, and the study of their different properties and relations. The student is, therefore, constantly engaged in observing the phenomena presented on submitting the different substances that come under his notice to the action of various agents, and in the accumulation of facts derived from experimental inquiry. It is, indeed, this circumstance which gives to Chemistry its principal charm; the tyro no sooner begins to *read* than he begins to make experiments, and being thus enabled, to a certain extent, to verify for himself the facts brought before him, he acquires an interest in his pursuit which attaches him daily more and more to it.

2. In order to pursue Analytical Chemistry with any chance of success, the student must possess certain qualifications; these may be stated to be—habits of strict order and scrupulous neatness; a dexterity of manipulation which practice alone can give; a firm conviction that the laws of nature are unchangeable, and that variations in experimental results must consequently imply either a non-fulfilment of certain necessary conditions, or some error in manipulation; and a rigorous

honesty, not only in recording results, but in experimenting, and in interpreting the phenomena which present themselves in the course of an investigation.

3. The determination of the constituent parts of a compound body is termed its *Analysis;* and this may be either of two kinds, according to the object which the operator has in view. If he merely seek a knowledge of the general nature of the substance, he is satisfied, when by the application of certain tests, and by the performance of certain operations, he has obtained evidence of the presence of those elements of which the compound is made up, and the analysis he performs is called *Qualitative;* but if he desire to appeal to the balance, and to ascertain not only the *nature*, but the actual *amount* of the elements present, he must shape his analysis in such a manner as to separate the constituents of the compound completely from each other, and obtain them either pure or in some other well-known form of combination: he then performs a *Quantitative* analysis. For example, if on the addition of a few drops of solution of ferrocyanide of potassium to a clear liquid a *blue* precipitate be obtained, the operator is at once satisfied of the presence of iron; and if he is working *qualitatively* only, this experiment is with regard to that particular element conclusive, it requires no additional confirmation; but if he desire to estimate the exact amount of iron present, he must conduct his analysis in such a manner as to separate every particle of the metal in the state of *sesquioxide*, in which state it is weighed, and the amount of metal deduced by calculation. Now, before the chemist can proceed to estimate the proportions of the constituents of a compound body, he must know exactly how many elements are present, and what those elements are. The *Qualitative* analysis always, therefore, precedes the *Quantitative;* and it will be necessary to separate the two courses of study, and to treat each individually.

QUALITATIVE ANALYSIS—OPERATIONS TO BE PERFORMED AND APPARATUS REQUIRED.

SOLUTION.

4. To prepare a substance for the exertion of chemical action, and to suit it for the reception of the various tests and reagents to which we may wish to submit it, recourse is always, if possible, had to solution. Now solution is of two kinds,

being effected either by fluids which exert no chemical action on the body dissolved, as when sugar is dissolved in water, or camphor in spirits of wine; or by fluids which *do* exert a chemical action on the substance, as when *chalk* is dissolved in *vinegar*, or *iron* in dilute *sulphuric acid*. Whenever it is practicable, the substance under examination is dissolved in water; but, if that menstruum should fail, recourse is had to other fluids, the selection of which requires care and judgment.

5. A compound may be made up of constituents, some of which are soluble in water, and some insoluble. In order to ascertain this point, a small quantity of the substance, brought into a fine state of division by pulverization, is introduced into a test tube covered with distilled water and submitted to heat; the liquid is filtered, while hot, into a small platinum or porcelain capsule, and evaporated carefully and slowly; if a residue remain, it of course indicates that a substance soluble in water existed in the compound. Should there be reason to suspect the presence of a volatile body soluble in water, heat should not be applied in the first instance, but the substance under examination repeatedly agitated with cold distilled water, and the clear solution allowed to evaporate spontaneously. Bodies, however, capable of assuming the gaseous state by the heat of boiling water, may in most cases be recognized by their odour, or by the application of certain tests which will hereafter be described.

6. *Alcohol*, *ether*, *pyroxylic spirit*, and certain *oils*, are occasionally successfully employed to dissolve substances on which water has no action; sometimes also a mixture of alcohol and water is found very useful. For example, if the object be to separate *sulphate of lime* (gypsum) from *chloride of sodium* (common salt), this cannot be effected by water alone, sulphate of lime being partially soluble in that fluid; but by employing a mixture of one part of alcohol and two or three parts of water the two substances are easily separated, sulphate of lime being insoluble in diluted spirit. Acids, again, sometimes act as mere solvents, and may be conveniently employed as such; thus *oxalate of lime* dissolves in *hydrochloric acid* without decomposition, as does also *phosphate of lime*, and both of these salts may be obtained again from their acid solution, unaltered by supersaturation with ammonia.

7. The apparatus required for the purpose of solution is in general very simple. For qualitative experiments there is nothing so convenient as the Test Tube. It should be made

of hard German glass, and the bottom blown round and tolerably thin. The student should possess a good stock of them: they should be of various sizes, from three to six inches long, and of such a diameter that they may readily be closed with the thumb, for the purpose of agitation. They should be kept ready for use in a rack, to which it is advisable that there should be attached a series of pegs on which the tubes may be inverted, to drain after being washed. If the tube-rack stand be provided with a couple of drawers, they will be found to add to its convenience: they serve to hold the blowpipe, platinum foil and wire, charcoal supports, fluxes, etc. etc. A spring-holder is a useful accompaniment to the test-tube apparatus; it serves to grasp the tube while its contents are under the influence of heat. When larger quantities of liquid have to be operated upon, flasks of various sizes may be substituted for test tubes. They should be of thin glass, with flattened bottoms and bordered mouths, ground smooth for the reception of corks, and to admit of being closed air-tight by ground-glass plates. The common Florence-oil flask is a useful chemical vessel; the edge of the mouth should be rounded in the blowpipe flame, whereby it is rendered less likely to crack by the insertion of a cork. It is, generally speaking, of very uniform thickness throughout, and will bear the direct application of heat without cracking. As a general rule, however, the naked flame of the oil, gas, or spirit lamp should not be allowed to come into actual contact with the bottoms of large glass vessels, but the heat communicated through the medium of sand; for this purpose a set of thin shallow iron dishes should be provided, from three to six inches in diameter, which should be about half filled with fine siliceous sand. They may be supported on the rings of a retort stand, and they then form very convenient media for conveying heat to flasks, beakers, etc. To support Florence flasks, and other round-bottomed vessels, rings of thin sheet-iron or copper, covered with list, will be found very serviceable: they should be of different diameters and heights; they are likewise of great use for supporting evaporating-basins, and the laboratory should, therefore, be plentifully supplied with them.

PRECIPITATION.

8. The term precipitation does not necessarily imply the subsidence of a solid substance to the bottom of a vessel, inas-

much as the body rendered insoluble may either float on the surface of the liquid, or remain suspended in it. When the chemist speaks of a body being precipitated, he means that it has, by the action of certain agents, passed from a soluble to an insoluble state. The body separated is called the *precipitate*, and the substance occasioning the separation is called the *precipitant*. The vessels employed for effecting precipitations may be the same as those already described for solutions, to which may be added the *beaker*, a thin-bottomed tumbler, which may be procured at any chemical glass warehouse, of all sizes, generally in nests of eight or ten from half a gill to a pint and upwards. For small quantities the test tube is always employed; when the quantity is large, the beaker is, on the whole, the most convenient, from the admirable manner in which it bears sudden elevations of temperature. Precipitates make their appearance in very different forms, and under very different circumstances. The student must, therefore, be careful not to draw too hasty conclusions with regard to the action which bodies exert on each other; and if, on bringing two substances into contact, he observe no immediate effect, he must not, on that account, conclude that no action has taken or will take place. A few examples will serve to illustrate this. 1st. The precipitate may not make its appearance until after the lapse of a considerable time. Thus, in testing for *magnesia*, by means of *phosphate* of *soda* and *ammonia*, if the earth exist in the solution only in very minute quantity, no precipitate will perhaps make its appearance for several hours; days may even elapse ere the minute stellar crystals of the double phosphate of magnesia and ammonia can be distinctly recognized. 2nd. Decomposition may have taken place, and yet, from the solubility of the educt in the fluid menstruum, no precipitate makes its appearance. Thus, on adding *oxalic acid* to a solution of *lime* in *hydrochloric acid* containing free acid, no precipitate appears, oxalate of lime being soluble in hydrochloric acid; but, on neutralizing the liquid by ammonia, oxalate of lime is immediately precipitated. Again, on adding to an aqueous solution of *malate of soda* a few drops of *chloride of calcium*, the fluid still remains clear, malate of lime being soluble in water, but on the addition of alcohol it instantly separates as a white powder. 3rd. Occasionally (though this is rare) the precipitate makes its appearance only on the application of heat, the newly-formed compound being more soluble

in cold than in hot water. Thus, on adding *lime water* to a cold solution of *citric acid*, or a *citrate*, no precipitate takes place till the solution is heated, when *basic citrate of lime* appears as a white powder, which redissolves as the solution cools: again, on adding a cold dilute solution of *caustic potassa* to newly precipitated *tartrate of lime*, a clear solution is obtained, but on heating, a gelatinous precipitate separates, which is again dissolved as the solution cools. 4th. The precipitated substance is frequently redissolved by an excess of the precipitant: thus, *hydrated oxide of chromium*, *hydrated oxide of zinc*, and *alumina*, are each thrown down from solutions of their salts by *potassa*, but the precipitates are all completely and instantly redissolved by the addition of an excess of the alkali: again, on pouring *iodide of potassium* into a solution of *chloride of mercury*, a beautiful scarlet precipitate immediately ensues; but, if excess of the iodide be added, the precipitate is dissolved, and a clear and colourless solution obtained.

9. The *forms* in which precipitates make their appearance have been distinguished by various names, such as *crystalline*, examples of which are furnished by the *acetate of silver*, a salt formed on adding solution of a neutral acetate to solution of nitrate of silver; by the *double chloride of platinum and potassium*, and by the *bitartrate of potassa*; *pulverulent*, as the *oxalate and sulphate of lime*; *flocculent*, as *alumina*; *curdy*, as *chloride of silver*; *gelatinous*, as when *oxide of zinc* is precipitated from its solution by *potassa* or *ammonia*, or as when *chloride of calcium* is added to an aqueous solution of *hydrofluoric acid*, or of the soluble *fluorides*, in which case the precipitate is so transparent that it may easily be supposed that no change whatever has occurred. Sometimes, again, a reaction is evinced by the mere turbidity of the liquid, as when *nitrate of silver* is added to a solution containing minute traces of *chlorine*, or when a solution of a *protosalt of tin* is diluted with *water*, in which case the neutral salt is decomposed into a soluble acid and an insoluble basic salt; or as when solution of *protochloride of tin* is added to a very dilute solution of *gold*, when a purple-red tint is produced without the formation of any precipitate. The subsidence of a precipitate is frequently greatly facilitated by agitation. In cases where an elastic substance is evolved by agitation, or where there is excess of ammonia present, the flask employed should not be too thin, or it will be liable to burst from the pressure of the vapour:

the addition of acids and salts also occasionally greatly facilitates precipitation; *chloride of silver* and *sulphate of baryta*, for example, separate much more readily by the addition of *nitric acid;* and *oxide of tin*, formed by the action of nitric acid on the metal, has its precipitation hastened by the addition of *common salt*. *Oxide of iron* again is sometimes eliminated in so finely comminuted a form that it remains suspended in the liquid for days; an addition of a known quantity of *nitrate of lead*, and a corresponding quantity of *sulphuric acid*, may often be very advantageously made to the turbid liquid; a known quantity of *sulphate of lead* is thereby introduced, which in its precipitation seldom fails to carry with it the whole of the suspended oxide of iron; lastly, *Prussian blue* precipitates from a solution containing free *hydrochloric acid* much more readily and completely than from a neutral liquid. In qualitative testing, where the object is generally merely to ascertain the colour and general chemical characters of a precipitate, a few drops of the precipitant usually suffice, and the operation may almost always be performed in a test tube: but in quantitative experiments, where every particle of the precipitate must be obtained, the precipitant is added drop by drop until no further effect is produced, and the operation is most conveniently conducted in a beaker.

FILTRATION, DECANTATION, AND WASHING.

10. The separation of a precipitate from the fluid in which it has been produced may be effected either by filtration or decantation. For the former purpose white unsized paper is used, the perfect purity of which in qualitative operations is not very often a matter of consequence: it should be sufficiently strong to bear the weight of a considerable quantity of fluid, and yet so porous as to admit the free and ready passage of liquids. There is no difficulty in procuring paper of this kind, though it is not easy to obtain unobjectionable paper for quantitative operations; for, as it frequently happens that the filter has to be ignited with the precipitate, it is of course necessary to take into account the quantity and quality of the ashes left by the paper. An excellent article is sometimes to be met with under the name of Swedish paper, a filter four inches in diameter of which does not leave more than a hundredth of a grain of ash. It is difficult, however, to procure it genuine, and it is therefore advisable to free paper

intended for minute and delicate experiments as much as possible from inorganic matter by treating it with hydrochloric acid, and subsequently washing with distilled water, so as to remove every trace of the acid: after drying, it may be considered fit for use. The inorganic impurities in filtering paper are iron, lime, and sometimes magnesia. The paper is cut into a circular form of the required size and folded twice in opposite directions, so as to bring the four quadrants together; one quadrant is then opened from the other three so as to produce a conical cavity, as shown in Fig. 1. The paper thus prepared is placed inside a glass funnel; care should be taken that it does not extend beyond, or even quite reach, the edge of the funnel. Previous to pouring the fluid to be filtered on the paper, the latter should be moistened with distilled water, which quickens the process and diminishes the chance of solid matter passing through the pores of the paper. In qualitative experiments where it is desirable to expedite the operation as much as possible, and in cases where a large quantity of a bulky precipitate has to be separated, the filtrate being the valuable part,—as for example, in the separation of the *alkaline earths* by baryta water in the process for estimating alkalies,—the filter may be plaited so as to prevent its close adhesion to the glass. Ribbed funnels are sometimes employed for the same purpose, but they do not answer the purpose nearly so well as plaited paper. It is difficult to describe the method of making these plaited filters: an inspection of Fig. 2, which shows the appearance the paper should present, will probably, however, convey all the requisite information. In cases where the precipitate has to be carefully collected, plain filters should invariably be used, as it is difficult to remove the solid matter effectually, from the external and re-entering angles of the plaited paper. The funnel, during the operation of filtering, is placed on the ring of the

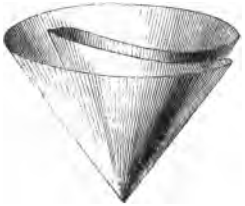

Fig. 1.

Fig. 2.

retort stand, or in one of the holes of a filtering-stand, and the fluid, if in a beaker, is carefully poured down a glass rod in the manner shown in Fig. 3. The edge of the beaker is greased, by which the adhesion of particles of the liquid is prevented, and all loss from trickling down the outside of the glass obviated. The clear fluid as it drops from the funnel should not be allowed to fall directly into the receiving vessel, but caused to impinge on its side, as shown in the figure; by attending to this, we avoid all chance of loss by the splashing of the liquid. These minutiæ of course principally apply to quantitative experiments. The precipitate, being collected on the filter, has to be washed. This operation is best performed by means of the wash bottle seen in Fig. 3, the

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method of using which useful piece of apparatus is sufficiently obvious; it is filled with distilled water, and on forcing a stream of air from the lips through the short tube, a jet of water is propelled from the bent tube by the pressure of the air, and may be directed either in drops or in a pretty power-

ful stream wherever it is required. It is useful to have four of these bottles at hand: one stout one, for cold water for general purposes; one made from a thin flat-bottomed flask, for hot water; and two smaller ones, for alcohol and ether. The washing of the precipitate is to be continued until a few drops of the filtrate leave no residue when evaporated to dryness on a strip of platinum foil; occasionally, however, this indication would be fallacious in consequence of the partial solubility of the precipitate in water; in these cases, special testing of the filtrate must from time to time be had recourse to. In washing a precipitate on a filter, the solid matter should be washed from the sides of the paper and collected, as much as possible, in a thick stratum at the apex of the cone; the water will not in this case pass through so quickly, but under more favourable circumstances for exerting its solvent power on the substances to be removed. During the operation of filtering, the funnel should be covered with a glass plate, to protect its contents from the dust and dirt of the laboratory. When the precipitate subsides rapidly and collects into a small space at the bottom of the vessel, the supernatant fluid may frequently be advantageously removed by a siphon, which may be made from a piece of glass tube about 2 feet long and 0·3 of an inch internal diameter. The extremities should be somewhat contracted. When this instrument is about to be used, it is filled with water from the wash bottle, and, keeping the longer leg closed by a finger, the shorter leg is introduced into the fluid, taking care not to disturb the precipitate, and then, on removing the finger, the fluid is permitted to run out into a vessel placed to receive it. With care, and by gradually inclining the vessel, nearly the whole of the clear fluid may be removed from a precipitate, the washing of which may either be continued by decantation, or, which in most cases is preferable, it may be thrown on a filter and washed as usual. In cases where small quantities of fluid have to be removed from a precipitate, the *pipette* is frequently found very serviceable. This is a narrow glass tube, with a bulb about an inch in diameter blown in it, and drawn out below to a moderately fine aperture. To use it, the aperture is immersed in the liquid, and the mouth being applied to the other end the liquid is raised by withdrawing the air; the finger being then placed on the upper end of the tube so as to close it, the instrument may be removed, and its contents transferred to another vessel. When the object is

to remove finely divided matter from concentrated acids, filters of powdered glass are employed; coarse fragments of glass are first put into the neck of the funnel, these are successively covered with other portions more and more comminuted, the top being finished by a layer of small fragments; on this the acid is poured, and, on passing through, it becomes clear. It is sometimes of importance to prevent the access of air as much as possible during the filtration of certain liquids, as, for instance, in the separation of *caustic soda* or *potash* from *carbonate of lime*. An apparatus for this purpose has been described by Mr. Donovan: it consists of a vessel somewhat resembling in shape an hour-glass provided with a tube of communication between each bulb; in the narrow part of this vessel a small pellet of cotton or asbestos is somewhat loosely placed, the liquid being introduced through the neck of the upper vessel, which is closed by a stopper; now, for every drop of liquid that passes through the filter into the lower vessel, it is obvious that an equal volume of air must find its way through the tube of communication with the upper vessel. The filtration of the liquid thus proceeds in an uninterrupted manner without any communication with the external air.

11. The precipitate, being collected on the filter and well washed, has in quantitative experiments to be dried and weighed; its further treatment for this purpose depends on whether or not it may be ignited. If its nature be such that it will not bear a high temperature without decomposition, which is the case with all organic substances, the filter must have been previously dried at the same temperature to which it is subsequently to be submitted with the precipitate, and in that state carefully weighed. As filtering-paper is a very hygroscopic substance, the filter must be weighed in a closed vessel (a platinum crucible, with an accurately fitting cover, may be used for the purpose); it must be introduced while hot, and it is advisable to allow the whole to cool over a vessel of sulphuric acid underneath a bell jar. The weight of the filter and crucible being noted, the precipitate is collected, and, the rinsing-water having been allowed to run off as much as possible, it is removed from the funnel, and placed upon two or three folds of bibulous paper, or, which is better, on a warm tile or brick, by which a great deal of the adhering water is removed; it is subsequently dried in the crucible until it ceases to lose weight, and by simply subtracting the

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7. The apparatus required for the purpose of solution is in general very simple. For qualitative experiments there is nothing so convenient as the Test Tube. It should be made

when the water boils it is driven off in steam at the rate of more than a gallon of water per hour. The method is consequently applicable to distillation on a small scale, and to numerous operations in pharmacy.

Arrangement for heating to Redness a large Fire-clay Crucible.—When a large crucible is to be heated to redness,—as, for example, when oxide of copper is to be dried for use in an organic analysis,—the gas-burner is to be used without the fire-box, *d*, Fig. 5, and is to be arranged with the furnace fittings that are represented in perspective by Fig. 9, and in section by the lower part of Fig. 12, *a*, *b*, *c*, *d*. Letter *a* represents the gas-burner, Fig. 5; *b* is a tall iron stool; *c*, a chimney which collects atmospheric air to feed the flame, and leads it up close to the vertical tube *b*, by which contrivance the air is warmed and the tube cooled; *d* is a furnace-sole or plate of fire-clay; *f* is a reverberatory dome, the interior of which is best shown in the section, Fig. 10; *e* is a cast-iron ring or trivet, represented more clearly in Fig. 11; *g* is an iron chimney, 24 inches long, and $3\frac{1}{2}$ inches wide; and *h*, a damper, to lessen the draught when small crucibles are to be heated. The height of this apparatus, from *a* to the top of *f*, is 24 inches; and the external diameter of the dome *f* is about 8 inches. The crucible, which may be from $4\frac{1}{2}$ to $4\frac{3}{4}$ inches in height, is placed on the iron ring *e*, and that on the clay sole *d*, and it is then covered by the dome *f*. The gas should be lighted after the crucible is placed in its position, and before the dome is put on. The dome and chimney are then to be added, and the operation allowed to proceed. With

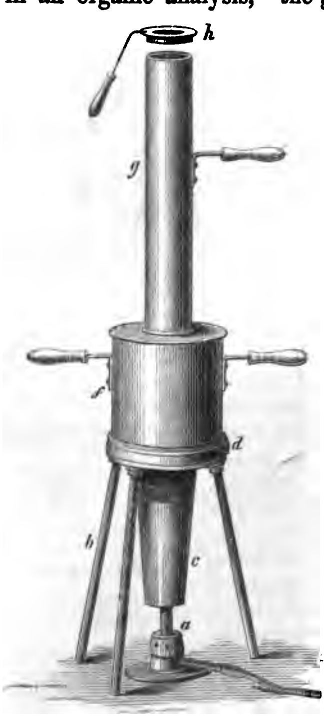

Fig. 9.

a crucible of the above size, the damper *h* is not required; but it must be used when the crucible is under 4 inches in height, otherwise the draught occasioned by extra space within the dome causes the flame to blow down. The damper must be put on the chimney before the chimney is put on the dome.

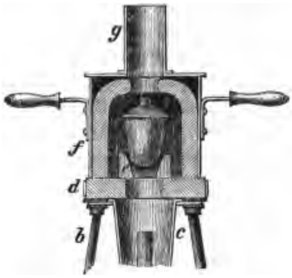

Fig. 10.

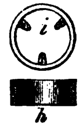

Fig. 11.

The iron ring, Fig. 11, or *e*, Fig. 10, suits crucibles of different sizes, according to the side of it which is turned uppermost.

The figures show that a crucible mounted in this furnace can lose very little heat by radiation or conduction, and hence it is that a small gas-flame produces a powerful effect. In half an hour a $4\frac{3}{4}$-inch clay crucible, filled and covered, can be heated to full redness. The progress of the ignition can be easily examined by lifting up the chimney *g* and the dome *f* by their respective wooden handles. But the action of the furnace can also be judged of by a peculiar roaring noise which it produces. If the gas and air are mixed in due proportions, the roar is regular and continuous. If there is too much gas, the roar is lessened. If too much air, the roar is increased, but is rendered irregular and intermittent. The greater the noise, the greater the heat in the furnace; but when the roar becomes spasmodic, the flame is on the point of blowing down. To prevent that occurrence, the proportion of air must be lessened or that of gas increased.

Arrangement for heating Platinum Crucibles, as in the Fusion of Silicates with Carbonate of Soda.—The following arrangement is convenient when small crucibles are to be strongly heated:—Anhydrous carbonate of soda in

quantities exceeding 1000 grains can be thus readily fused, and small quantities of sterling silver can be melted in a clay crucible. It is also available for ignitions or fusions in small porcelain crucibles. Fig. 12 represents the arrangement of apparatus as seen in section. *a* is the gas-burner; *b*, the stool; *c*, the air-chimney; and *d*, the furnace sole, as already explained. *i* is a cylinder of fire-clay, 4 inches high and 4½ inches diameter; *k* is a plumbago or fire-clay furnace, in which is placed a small cast-iron ring, similar in form to that represented by Fig. 11, and on this ring the platinum crucible is adjusted; *l* is a fire-clay or plumbago reverberatory dome; and *g* is the chimney that forms part of the furnace represented by Fig. 9. The crucible being adjusted, the gas lighted, and the dome and chimney put on, the lapse of twelve or fifteen minutes, according to the quality and pressure of the gas, suffices for the fusion of 1000 grains of carbonate of soda in a platinum crucible.*

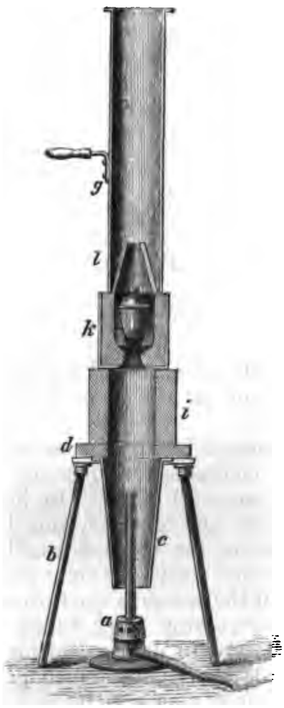

Fig. 12.

It will be noticed in Fig. 12 that the crucible is placed very high above the orifice of the tube *a*, at which the gas is inflamed. The distance is, in fact, about ten inches, the point of maximum heat in the flame being at nearly that distance from the burner, more or less, according to the pressure and the quality of the gas. The gas which rises from the burner *a*, though mixed with as much air as it will bear without becoming explosive when lighted, does

* If this quantity of fused carbonate of soda be permitted to cool and consolidate in a platinum crucible, the salt is liable to expand and burst the crucible.

not contain sufficient oxygen to burn all the carbon present in it. The flame produced is, consequently, quite superficial. The gaseous mixture only burns on the surface where it is in contact with fresh atmospheric air, and it requires time to take up the requisite amount of oxygen. The draught produced by the joint action of the two chimneys *c* and *g* carries the flame rapidly to a great height before the point of complete combustion is attained.

When the highest degree of heat is not required, the reverberatory dome *l* may be omitted. It must also be dispensed with when the crucible that is to be heated is of comparatively large size, because it is then liable to lower the temperature of the furnace by impeding the draught.

The effects that have been ascribed to the various arrangements of this gas-furnace can be produced with gas supplied by a pipe of a ½-inch bore, and at a moderate pressure giving from 30 to 40 cubic feet per hour.

The principles of heating by gas, which have led Mr. Griffin to the construction of this furnace, may be summed up as follows:—When a crucible or other solid body is to be heated, it is to be wrapped in a single flame at the point of maximum heat, and loss of heat by radiation and conduction is to be prevented by the interposition of non-conducting materials (plumbago or fire-clay); and when liquids are to be boiled or evaporated, particularly when they are contained in vessels of glass or porcelain, the flame is to be broken up into numerous horizontal jets, and these are to be made to supply a large and regular current of highly-heated air, by which alone, and not by the direct application of the flame, the vessel that contains the liquid is to be heated. In both cases provision must be made to secure a sufficient draught of air through the furnace, because every cubic foot of gas requires for combustion 10 or 12 feet of cubic air, and the gases which have done their duty must be rapidly carried away from the focus of heat. If the steam, the carbonic acid gas, and the free nitrogen, which constitute the used-up gases, are not promptly expelled, fresh gaseous mixture, in the act of producing additional heat by combustion, cannot get near the object that is to be heated, and the heat so produced out of place is wasted.

15. *Normandy's Gas Blowpipe Furnace.**—This is shown in

* Normandy's Chemical Atlas, p. viii.

Fig. 13. It consists of a wire-gauze cylinder partly cased in sheet-iron, in communication at the lower part with the atmospheric air, closed at the upper part by a diaphragm of wire gauze of about 700 openings to the square inch, and provided with a short, slightly conical cover, perforated in the centre. A blow-

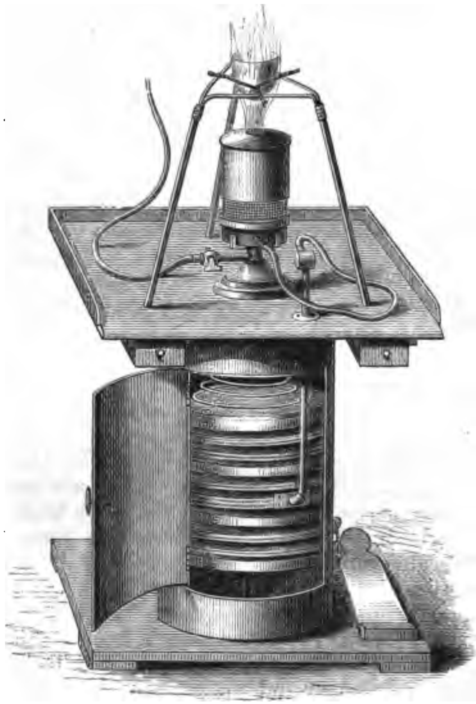

Fig. 13.

pipe jet, placed outside the cylinder, traverses the diaphragm, and opens on a level with the aperture of the cover; a blast of air is sent into the centre of the flame by means of a flexible tube of vulcanized caoutchouc from a bellows, as shown in the figure, a flame is thus produced of very great intensity, and well adapted to most of the requirements of the laboratory.

16. Where a supply of gas cannot be obtained, the chemist

must have recourse to spirit-lamps or furnaces for the ignition of his crucibles. A useful form of Berzelius's spirit-lamp is shown in Fig. 14; the reservoir containing the spirit

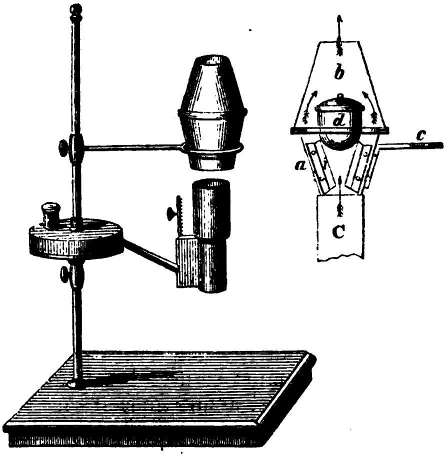

Fig. 14.

being at a distance from the burner, it escapes being heated during long operations. Fig. 15 represents a lamp of Russian invention, by which a powerful heat may be obtained in a few minutes. It consists of a strong double brass cylinder or box; the dotted lines in the figure show the arrangement of the interior; a piece of tube terminating in a jet passes from the exterior to the interior chamber, rising nearly to the top of the former; the fuel (spirit) is supplied through the aperture, *b*, which should be closed with a good cork, and

Fig. 15.

never with a brass cap, with which the instrument is sometimes

sold. To give the lamp its maximum charge, the spirit should be poured in until it begins to flow out from the jet; a sufficient quantity should then be poured into the inner chamber, to reach within half an inch of the apex of the jet. The principle of the lamp will now become obvious. On inflaming the spirit in the inner chamber, that in the outer chamber gets heated and soon boils; the pressure of the vapour forces the boiling spirit through the jet in a powerful stream, which of course becomes immediately ignited, and thus acts as a powerful blowpipe; and so great is the heat produced, that a platinum crucible, placed in the position shown in the figure, speedily becomes ignited to whiteness. A platinum triangle must be used to support the crucible, as an iron one would speedily become destroyed. A lamp on this construction, about 3½ inches in height, and 3½ inches in diameter, will burn with a charge of 4 oz. of spirit for thirty minutes, which is long enough for all ordinary fluxions with carbonate of soda; it frequently, therefore, saves the necessity of lighting a furnace. In using this lamp certain precautions must be used before giving it a charge of fuel. The operator must assure himself that the jet or pipe is not choked up by blowing through it; the cork at *b* should not be put in too tight, in order that it may be the part of least resistance should a stoppage occur during an operation; and lastly, the cork should be turned from the operator during an experiment, to secure him from accident should it get blown out by a stoppage.

Besides these different forms of lamp, the common twisted cotton-wick spirit-lamp is a very useful instrument; a very considerable degree of heat may be obtained from it; and small platinum crucibles may be heated to redness in its flame. The heating power of all these lamps is greatly increased by enclosing the crucible in a jacket of iron plate, as represented in Fig. 14. Professor Sainte-Claire Deville has contrived a lamp, in which the combustion of spirit of turpentine is effected with the assistance of a blast of atmospheric air, and the result is the production of a high degree of heat. (See Griffin's 'Chemical Recreations,' pp. 582–3.)

17. *Furnaces.*—The varieties of furnaces that have been contrived by different chemists for particular and for general purposes are almost innumerable, and it would require an entire treatise to descant on their several uses and comparative merits. In the well-appointed laboratory, the wind, blast, and reverbera-

tory furnaces will of course find their proper places; but, as it is no part of our object in this treatise to give a minute description of the apparatus required in a large chemical establishment, we shall merely notice one or two of the furnaces which seem best adapted to small private laboratories, and for the use of students in analytical chemistry.

A very useful furnace may be made out of a black-lead or "blue" pot; one of those vessels, about a foot in height and seven or eight inches in width at the top, will make a furnace quite large enough for the ignition of small crucibles, and for operations on the small scale. It should have a series of round holes pierced in it at equal distances apart round the side for the admission of air, and it should be tightly bound round with stout iron or copper wire to strengthen and hold it together when it cracks. A small cast-iron grate resting between the bottom and the second tier of holes, and a moveable hood or chimney, complete the apparatus. "There is no difficulty," says *Faraday*, "in raising a crucible two inches and a half in diameter to a white heat by a furnace of this kind; and that, in any situation which may be convenient upon the table or the floor, and with all the advantages of arranging or dismounting the apparatus with extreme facility." One of the greatest recommendations of this furnace is its extreme cheapness, the entire cost not exceeding a few shillings. Minute directions for constructing it and arranging it for different operations will be found in Faraday's 'Chemical Manipulation.'

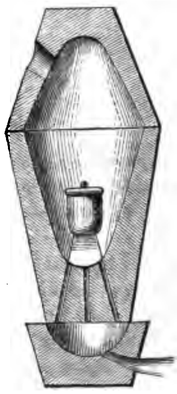

Fig. 16.

Fig. 16 represents Mr. Aikin's portable blast furnace. Like the one last described, it is made generally out of black-lead pots, three being used for the purpose. The lower part of the first one serves as a resting-place for the body of the furnace; it has a hole drilled through it, by which air is supplied from a bellows to the body of the furnace, which is another crucible placed above the lower one, in which several holes are drilled to admit air; over the second crucible a third is inverted, with a large hole cut in the side for the escape of smoke and gaseous matters. Cast-iron may be melted in this furnace, and moderate-sized crucibles

brought to a full red-heat in a few minutes. The fuel used is coke.

Fig. 17 is known as *Black's* furnace, and is, perhaps, on the whole the most convenient where a stationary furnace is required. It consists of a case of strong sheet-iron lined with refractory clay, the grate is fixed to the iron plate which supports the tube, and forms the top of the ash-pit, which is provided with a sliding door for the admission of air; there are various apertures in the front and sides of the furnace for the admission of tubes, crucibles, etc. The fuel used is coke.

Fig. 17.

18. *Crucibles.*—By this name are designated those vessels in which substances are subjected to high temperatures. They vary considerably in material as well as in shape. Those most commonly employed in the laboratory are the following:—

The *Hessian crucible*, to which preference will almost always be given where earthen vessels are required. They are triangular in shape, and will resist a high temperature, as well as the action of fluxes. They are not provided with covers, and are sold in nests of five or six, at a very moderate price.

The *Cornish crucible.*—They are generally round, and are provided with covers. In power of resisting high temperatures, and the action of fluxes, they nearly equal the Hessian, from which they are distinguished by their colour being white.

The *Blue pot*, or *Black-lead Crucible.*—These vessels are made of a mixture of black-lead and clay, and are generally of a large size, being principally used in the arts. They bear a very high temperature, and withstand the action of fluxes.

Crucibles made of *Berlin ware, biscuit porcelain*, and *Meissen ware*, are also much used. They are made very thin, and will

stand a high temperature; the most convenient shapes are shown in Figs. 18 and 19. Besides these, a crucible and cover of *platinum* is indispensable to the analytical chemist. This valuable vessel should be used with care; it should never be exposed unprotected to the fuel of a furnace. In almost every case a sufficient heat for all analytical operations may be obtained by gas, but when a very high temperature is required, and it is found necessary to resort to the furnace, the platinum crucible should be inserted into a Cornish one, the intervening space being filled up with lime. A pure silver crucible may in many cases be substituted for one of platinum; but it must be borne in mind that silver is far more fusible than platinum. Fusible metals, or compounds of metals likely to be reduced, must never be heated in vessels of silver or platinum, as the alloys formed greatly injure them: all compounds containing lead must also be particularly avoided. Our limits do not allow of our entering into the details of furnace operations. The student will find the subject fully treated in Faraday's valuable work on 'Chemical Manipulation.'

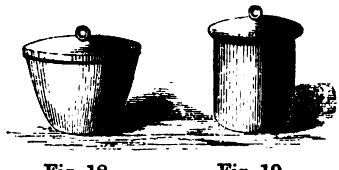

Fig. 18. Fig. 19.

THE BLOWPIPE.

19. For submitting small substances to high temperatures, and for obtaining a knowledge of the materials of which they are composed, the blowpipe is an invaluable instrument, and one with the use of which the chemical student should spare no pains to make himself thoroughly acquainted.

The blowpipe, though the forms which it has received are very numerous, is essentially a tube terminated by a small, round, smooth aperture, through which a current of air can be propelled by the mouth against the side of a flame. A miniature blast-furnace is thus set in action; and not only may an intense white heat be produced and directed against the subject of experiment, but several distinct operations may be performed on it, as will presently be shown.

The most simple form of blowpipe is a conical tube of japanned tin-plate or brass, about seven inches long, bent nearly at a right angle, about two inches from the narrow end;

but as, during the operation of blowing from the mouth, aqueous vapour condenses, and is driven through the jet with the stream of air, various contrivances have been devised for retaining the water.

Dr. Black's blowpipe, which is the cheapest, and, on the whole, perhaps the most useful of the numerous forms which have been given to this instrument, is shown in Fig. 20. It is a conical japanned tin-plate tube, two-fifths of an inch wide at the broad end, which is closed, and one-third of an inch wide at the narrow end, which is open. A small brass pipe, terminated by a jet two inches long, and one-eighth of an inch in diameter, is adapted to the side of the tube near the broad end. The moisture from the breath is condensed and retained at the closed end, the conical form of which serves also, in some degree, to regulate the pressure of the air.

Fig. 20.

The principal point to be attended to in the construction of the blowpipe is the jet, of which there should be two, the calibre of the one being rather larger than that of the other; the aperture should be perfectly round and smooth, and the channel leading to it conical; and it should be made of platinum, as being easier kept clean. In using the blowpipe, the air is supplied from the mouth, and not from the lungs; and during the blast the communication between these two organs is closed, respiration being carried on through the nostrils. The description of the method of blowing through the pipe is far more difficult than its acquisition. It is necessary, in the first place, to acquire the means of keeping the cheeks distended with air, whilst respiration goes on in an unimpeded manner through the nose; and to open and close the communication between the mouth and the lungs, and between the lungs and the air at pleasure. When this habit is gained, no difficulty is experienced in keeping up a strong and continuous stream of air without fatigue or injury to the health.

The fuel for supplying the flame for the blowpipe may be either that of a candle with a thick wick, or oil, or a solution of oil of turpentine in spirits of wine, or gas. The latter, when it can be obtained, is the most convenient; and Griffin

(see 'Chemical Recreations') recommends that the form of the burner should be that of a flat pipe, about 1½ inch wide, and ⅛ of an inch broad, cut aslant at an angle of 40° from the horizontal. When oil (which should be olive or refined rape) is used, the best form of lamp is that used by Berzelius, Fig. 21.

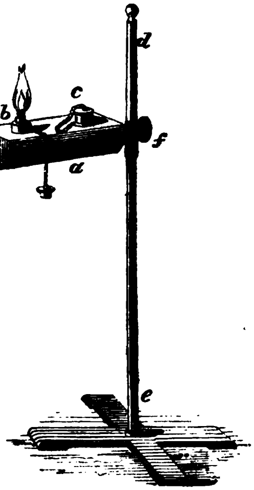

Fig. 21.

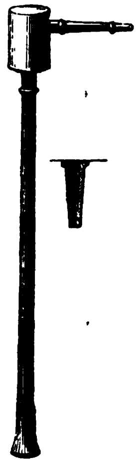

Fig. 22.

The vessel containing the oil, *a*, is adapted to a vertical support, *e d*, on which it may be adjusted, at any convenient height, by the screw, *f*. The oil-vessel is furnished with two apertures, *c* and *b*, each of which may be closed by a cap; the fuel is supplied through *c*, and the wick is introduced through the aperture, *b*. Fig. 22 is the form of blowpipe employed by *Plattner*. If a candle be employed, it should be snuffed rather short, and the wick turned on one side towards the object, so that a part of it may lie horizontally; the stream of air from the blowpipe must be blown along the horizontal part as near as possible without striking the wick.

20. *Structure of Flame.*—To understand the method of managing the blowpipe requires the knowledge of the properties of the different parts of a flame, which may best be studied in that of a steady-burning candle. Fig. 23 represents such a flame,

which will be found, on examination, to consist of four distinct parts. The base, *d d*, is bright blue; it is here that oxygen enters the flame; the blue colour, which is produced by the thorough combustion of the carbon of the fuel, disappears as the flame elongates, giving place to a thin, scarcely visible coating, *b b*. Chemical action is here most intense, and this exterior mantle is the hottest part of the flame. In the very centre of the flame, surrounding the wick, is a dark, conical spot, *a;* this is the magazine, as it were, of the inflammable gases derived from the decomposition of the tallow; it is shut out from all communication with oxygen, and the combustible gases consequently remain unburned. Surrounding this dark portion is an intensely luminous envelope, *c c*. It is here that the inflammable compounds of carbon and hydrogen are decomposed; the hydrogen burns into water, but the carbon, not meeting with a sufficient supply of oxygen to effect its oxidation, separates in a state of intense ignition. A few simple experiments will serve to elucidate the above description.

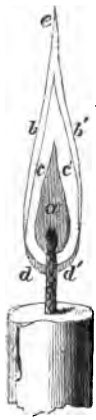

Fig. 23.

The hollow structure of the flame is proved by bringing down upon it a piece of thin glass or wire-gauze, and viewing the section of the flame from above. That this hollow is filled with inflammable gases is demonstrated by carefully introducing into its centre a piece of thin glass tube one-eighth of an inch in diameter, and six or eight inches long: the gases will escape through this tube, and may be inflamed at its exterior aperture. That the luminous part of the flame consists of intensely ignited charcoal is shown by introducing into it a cold body, such as a plate, which will become blackened from the deposition of carbonaceous matter. That the blue colour at the base of the flame is occasioned by the combustion of some form of carbon, is proved by holding close to it a glass rod, from the end of which a drop of lime-water is suspended—the clear liquid speedily becomes milky, owing to the formation of carbonate of lime; and, lastly, that the hydrogen of the fuel is being converted into water at the exterior envelope is rendered evident by holding near it a large bright metallic surface, such as a polished snuffer, which speedily becomes bedewed with moisture. Of these four parts of the flame *two* are principally concerned in blowpipe operations—the blue part

and the luminous part; and these two have totally different and indeed opposite functions. From the first is produced the *oxidizing* flame, and from the second the *reducing* flame. The *oxidizing flame* may be considered as the blue oval base converted into a cone. To produce it, the nozzle of the blowpipe is introduced about one-tenth of an inch within the flame, immediately above the wick, and a gentle and uniform current of air kept up from the mouth. The heat is greatest at the extremity of this flame; but to obtain the greatest oxidizing power, the subject of experiment should be kept as far from the apex of the flame as is consistent with a sufficiently elevated temperature. A too powerful blast must be avoided, as tending to cool the flame and to injure the process of oxidation: the aperture in the nozzle of the blowpipe must not be too small.

Fig. 24 shows the form which the flame should assume when oxidizing effects are desired; the blue dart, *a*, *b*, is the lower blue exterior part of the flame in its natural state, now concentrated in the interior. The *reducing flame* is more difficult to obtain; the jet of the blowpipe must not be introduced into the flame, but kept just on its edge, and the stream of air, thrown higher over the wick than in the oxidizing flame, the whole of the luminous portion thus becomes deflected, and appears as a long narrow cylinder surrounded by a feeble luminous mantle. It is in the luminous portion, consisting of partially consumed combustible matter, strongly disposed to combine with oxygen, that reductions are effected, and the assay must be entirely surrounded with it. Fig. 25 may serve to convey some idea of the general appearance of the reducing flame. If a lamp or candle be used as fuel, attention must be paid to the condition of the wick,

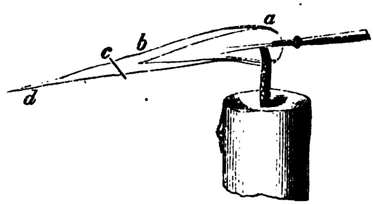

Fig. 24.

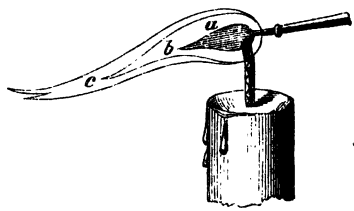

Fig. 25.

which must be of moderate length, and very evenly and smoothly cut. The orifice in the jet of the blowpipe should be smaller than when oxidation is the object, the blast must be moderately strong and uninterrupted. For the purpose of acquiring practice, the student should fuse a minute quantity of *oxide of manganese* with borax, upon a platinum wire in the oxidizing flame, when a violet-red glass will be obtained; by submitting this glass to the reduction flame it will become colourless, or nearly so, according as the flame has been made more or less perfect. Or a piece of *tin* may be fused upon charcoal, and kept in that state for a considerable time, while it presents the appearance of a bright metal on the surface: this will require dexterity in the operator; for if the oxidation flame should chance to touch the bright metal only for a moment, it becomes coated with an infusible oxide.

21. *Blowpipe supports.*—Objects are supported before the blowpipe either on charcoal or on platinum. When the subject of experiment has to be heated with free access of air, in order to see whether any volatile matters are given off, the operation is conducted in a glass tube open at both ends. The best charcoal for blowpipe operations is made from the wood of pine, willow, or alder; it should be well burned and free from bark. *Griffin* recommends that a supply of capsules of charcoal should be kept ready for use; he directs them to be made thus:—Take sticks of an inch in diameter, or, if the charcoal be in thick masses, cut it into sticks an inch square with a fine saw. Next, cut these sticks crosswise into flat pieces one-third of an inch thick, and make in each plate a cavity one-tenth of an inch deep, and one-fourth of an inch wide, to serve as a species of capsule to hold the substance to be heated. These capsules are held in the fire by a narrow and thin strip of tin plate.

As there is some difficulty in procuring unexceptionable charcoal for blowpipe experiments, *Mr. Griffin* has described and recommended ('*Chemical Recreations*') the following simple methods of preparing supports for *fusions* as well as for operations of *reduction*:—Into a small boxwood mould there is first pressed a plastic mass made of fine pipe-clay and charcoal powder mixed in equal parts, by weight, with as much water slightly thickened with rice-paste as is sufficient to form a stiff plastic mass. This forms a conical cup or crucible. On this is firmly pressed, by means of a suitable

boxwood pestle, a round ball of either of the combustible compositions described underneath; the whole forms a small cylinder half an inch high, and half an inch in diameter at the top, and about two-fifths of an inch at the bottom: it weighs about 16 grains, consisting of 10 grains of clay, and 6 grains of combustible matter. The little cylinder is easily removed from the mould by means of the pestle, which, as well as the inside of the mould itself, should be oiled.

The combustible portion of the support for *fusions* is made of

Charcoal in fine powder	12	parts
Rice-flour	$\frac{1}{2}$	"
Water, about	8	"

The rice is boiled with water to form a paste, with which the charcoal is afterwards mixed, into a mass of the consistence of dough.

The upper part of the support for *reductions* is made of

Charcoal in fine powder	9	parts.
Carbonate of soda, crystallized	2	"
Borax crystallized	1	"
Rice-flour	$\frac{1}{2}$	"
Water, about	8	"

The water is boiled, the soda and borax are dissolved in it, and the rice is then added to form a paste, with which the charcoal is finally incorporated, and the whole well kneaded into a stiff mass.

In using the support for fusions, it is heated before the blowpipe till it is red-hot, and on removing it from the flame it continues to glow like a pastile, and would consume entirely away down to the clay mixture. A quantity of microcosmic salt is now added, which immediately melts into a small cavity bored in the centre of the support, forming a bead, which is heated in the blowpipe flame till it becomes transparent and colourless. It is now removed from the flame, and placed on a Berlin capsule; the subject of experiment is added, and, as in consequence of the glowing state of the support the flux remains in a pasty condition, the added substance is immediately absorbed. It is again fused before the blowpipe, and on removing it the pastile burns gradually away, leaving the bead on the clay support, where it may be conveniently examined.

In using the support for reductions it is first heated before the blowpipe: as the charcoal consumes, the fluxes fuse and become concentrated on the surface; and on heating a reducible

metallic compound upon it, it becomes immediately exposed to a powerful reducing action.

These forms of support have certainly the merit of great portability, and are, therefore, well adapted to the travelling mineralogist. The whole of the apparatus may be purchased of *Mr. Griffin, of Bunhill Row*, for a few shillings. Rice is chosen as being a strong, cheap, and convenient agglutinant melting and binding the charcoal powder well together, and yielding itself, by its decomposition, a charcoal of difficult incineration. The supports are held before the blowpipe on a ring of iron wire thrust through a cork.

When charcoal is employed, for nearly all ordinary operations, the cavities may be bored in it by means of a simple conical tube of tin plate, the edges of which are sharpened by a file; the diameter of the small end may be one-fourth of an inch, that of the large one, one-half. A very ingenious charcoal furnace for quantitative blowpipe operations will be found described, though not so clearly as could be desired, in the valuable manual of Plattner.

Charcoal is employed as a support when the subject of experiment has to be reduced; but when the object is to ascertain what coloured bead it produces when fused with borax or microcosmic salt, a platinum wire curved at one end may be advantageously employed. It should be about two inches long, and it may be fixed in a hilt, the handle of which is hollow, serving as a reservoir for extra wires. In using these wires the hook is moistened in the mouth, and then dipped into the pounded fused borax, which is melted in the flame into a clear bead; when cool it is again moistened, a minute quantity of the substance to be examined caused to adhere to it, and both fused together.

22. It is frequently required to heat the substance with nitre or bisulphate of potash; this is done in the small platinum spoon, Fig. 26, of which it is convenient to have two sizes—one about nine-sixteenths of an inch in diameter, for melting substances with bisulphate of potassa; and the other about three-eighths of an inch in diameter, for fusing substances with nitre. Stains on these spoons are best removed by rubbing them with charcoal powder. In order to try the fusibility of a specimen, it is held in the flame by

Fig. 26.

means of the platinum forceps, Fig. 27. The following simple method of preparing small thin clay basins for roasting ores

Fig. 27.

and for the reduction of lead and tin oxides contained in calcined and uncalcined minerals, etc., is given by Plattner. A fine proof-clay is kneaded into a stiff paste with water, and having rubbed the surfaces of the boxwood press, Fig. 28, with oil, a slip of paper three inches in length and one-fourth of an inch in breadth is placed on the middle of the concavity of the press, which is seven-eighths of an inch wide and five-sixteenths of an inch deep, and upon this a small clay-ball about half an inch in diameter; the upper surface of the press is then stamped horizontally on the clay mass as far as is required. This being done, the superfluous clay will have exuded, and the handle or upper part of the apparatus can be removed easily by careful turning; with a small knife the clay which is driven out may be cut away, and it can then be seen whether the basin is sufficiently thin and uniform; if so, the slip of paper is gently pulled and the dish extracted. After a few hours' drying, the paper detaches itself from the little clay dish, which is then heated to redness in a platinum crucible. These basins should not exceed one thirty-second of an inch in thickness, and the proper consistence of the clay is soon ascertained: if the edges of two of these little vessels be ground with a file, one may serve as a cover to the other.

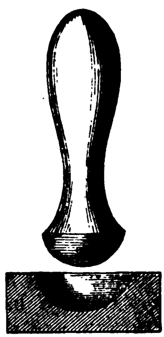

Fig. 28.

The steel mortar, Fig. 29, is an apparatus of great use to the blowpipe and mineral analyst. It consists of three separate parts: the lower portion is a shallow dish of steel into which a massive hollow hemispherical

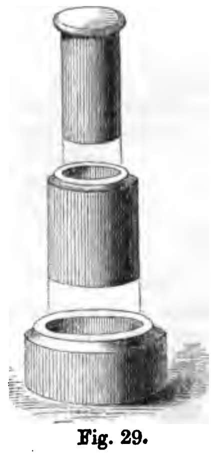

Fig. 29.

cylinder, also of steel, is accurately fitted by grinding; the upper portion is a solid cylinder of the same metal, which exactly fills up the hollow cylinder. When a mineral has to be crushed, it is introduced into the bed of the mortar, the solid cylinder is then replaced and struck forcibly several times with a mallet, by which it is reduced to a coarse powder, and may afterwards be brought to an impalpable state by grinding in the agate mortar.

EVAPORATION.

23. Evaporation is an operation to which the chemist is constantly resorting; he has recourse to it for concentrating liquids previous to the application of certain tests; for separating volatile fluids from fixed substances; for inducing crystallization; or for obtaining in a solid form substances held in solution by water or other liquids. When the object is to retain the fluid evaporated, as well as the residue, the process is called *distillation*. The ordinary operation of evaporation is conducted in basins of earthenware, silver, or platinum: watch-glasses also occasionally form very useful vessels. The earthenware basins should be as thin as is consistent with strength, and should resist the action of acids and alkalies in solution; the silver and platinum vessels should be provided with a projecting slip of metal to serve as a handle, whereby they may be held by a pair of pincers. In ordinary cases, the object sought by evaporation is attained by exposing the fluid to heat; sometimes, however, it is effected by leaving it for a certain time in contact with the atmosphere at common temperatures, or in confined air kept dry by hygroscopic substances. In *quantitative* experiments the evaporating substance should never be allowed to enter into actual ebullition, as a loss would almost unavoidably be sustained by bubbling. It is frequently advisable, therefore, to apply heat through the medium of the water bath, which may be a copper basin about six inches in diameter and three inches deep, provided with a series of rings of different diameters to suit dishes of different sizes. While a liquid is evaporating, it is requisite carefully to protect it from dirt and dust: this is best done in the manner recommended by Fresenius, viz. by providing two small, thin, wooden hoops, one of which must be made to fit loosely in the other; a sheet of blotting-paper is spread over the smaller, and the larger pushed over it: an excellent cover is thus formed, which,

while it effectually guards the liquid, does not come into contact with it, and does not in the least impede or retard the process of evaporation. Sometimes it is necessary to evaporate fluids from solid substances contained in crucibles: in such cases the crucible should be supported in an inclined position, and the heat applied a little above the level of the liquid: an equal distribution of heat is thereby secured, and the loss of a portion of the sediment by spirting avoided. The same method may be adopted in the evaporation of solutions of those salts which have a tendency to effloresce and creep up the sides of the evaporating vessel: in the latter case the object may be also attained by slightly greasing the upper part of the sides of the dish. Very frequently in the course of an analysis large quantities of filtrates have to be evaporated down to perfect dryness: in such cases the fluids are first concentrated by evaporation over the naked fire, and afterwards transferred into smaller vessels, to be finished in the water or sand bath. The process of transferring liquid from one basin to another, so as to avoid the smallest loss, requires care and a steady hand; the edge of the large dish should be slightly smeared with tallow, and the liquid poured down an inclined rod, as recommended above when treating of filtration. The evaporation of a mineral water from which carbonic acid or other gases are expelled by heat, should alwavs be commenced in a flask loosely covered with a piece of bibulous paper.

As the evaporation of a fluid in which a considerable sediment is formed draws to a conclusion, the thick mixture requires to be treated with great care; for, the circulation of the heat being now interrupted, the temperature frequently increases at the bottom of the vessel until above the boiling-point of the solution, and then the sudden evolution of small quantities of steam occasions a projection of portions of the substance from the basin. Sometimes, indeed, when the solid residue dries hard, it forms a cake on the surface, underneath which steam accumulates, and suddenly explodes with a force not merely sufficient to disperse the contents of the vessel, but even to break it in pieces. In these cases, the substance should be continually stirred with a glass rod, by which the loss by spirting is prevented.

DISTILLATION.

24. This operation is performed when it is desired to collect

the evaporating substance. It must obviously, therefore, be conducted in an apparatus in which the vapour as it rises may be refrigerated, and again reduced to a liquid or solid state, and collected in a separate vessel. When the elastic fluid or vapour assumes on cooling the solid state, the process is called *sublimation.*

The vessel in which almost every laboratory distillation is effected is the glass retort; those made of hard green glass are the most serviceable, as they withstand the action of caustic alkalies; it is difficult, however, to get them stoppered. Retorts made of hard German glass are now much used in this country; their high price, though lately much reduced, is the only objection to be raised against them.

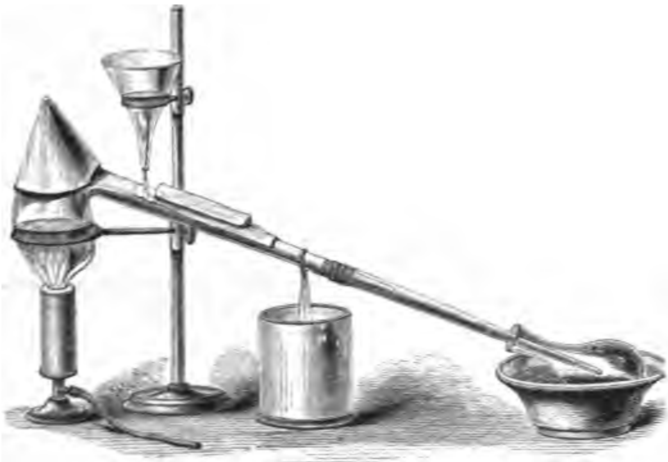

Fig. 30.

The general process of distillation is represented in Fig. 30. The bend of the retort is protected from the cooling influence of the air by a thick paper or cardboard cone, with a broad notch to admit the neck; this interferes with a ready change of air at the top of the retort, and saves much heat which would otherwise escape at that part, from the condensation of the vapour within. The end of the neck of the retort is connected with a long tube, either by means of a cork or occasionally by

cement, or loosely, the junction being made tight by strips of moistened bladder or sheet caoutchouc, and the end of this tube enters the mouth of the vessel into which the distilled products are to be received. The receiver is plunged into a basin of cold water in which lumps of ice are floating. In order to liquefy the vapour rising from the retort as soon as possible, several folds of bibulous paper are wrapped round the neck, just below the bend; and lower down, just above the point where the neck enters the adapter, a ring of tow is tied, the ends of which are caused to hang down four or five inches. Cold water is supplied to this paper from a large funnel containing a filter placed immediately above it in such a position that the drops of water shall fall on and spread over the paper, which will soon become saturated, and the water will run down to the tow, from which it will descend and be caught in a vessel placed beneath, and, provided it does not flow in too rapid a stream, none will enter the flask.

In the distillation of many liquids, particularly such as contain alcohol, the vapour is frequently evolved with such difficulty as not only to endanger the sudden expulsion of part of the substance, but the safety even of the whole apparatus. A tranquil and regular evolution of vapour may always be obtained by introducing into the retort certain angular solids on which the liquid exerts no chemical action, as fragments of glass, or, still better, slips of platinum foil; but care must be taken not to introduce these promoters of evaporation while the fluid is *hot*, or the burst of vapour might probably be so instantaneous as to do more harm than the previous irregular boiling. The same precaution is applicable to the introduction of solids, of whatever nature, into liquids while boiling or near their boiling-points. Sulphuric acid, which is the most difficult and dangerous of all substances to distil, may be drawn over quietly and regularly by previously dropping into the retort a few pieces of platinum foil or wire.

Various other contrivances have been resorted to for the purpose of condensing the vapour in the process of distillation. In the common still, this is well known to be accomplished by causing the vapours to pass through a long spiral tube, called a *worm*, fixed in a tub, and surrounded by cold water. In cases where the products are not easily condensed, *Liebig's condenser* is a very useful and convenient arrangement, and is applicable in all cases where an open apparatus is admissible.

The condenser is a hollow metal cylinder, through the centre of which a glass tube passes, being fixed water-tight by means of perforated corks covered with cement. This tube is connected either by a cork or by tubing with the beak of a retort; a constant stream of water is caused to flow from the reservoir placed above, down the funnel, thus entering the cylinder at its lower part. The water, warmed by the condensation of the

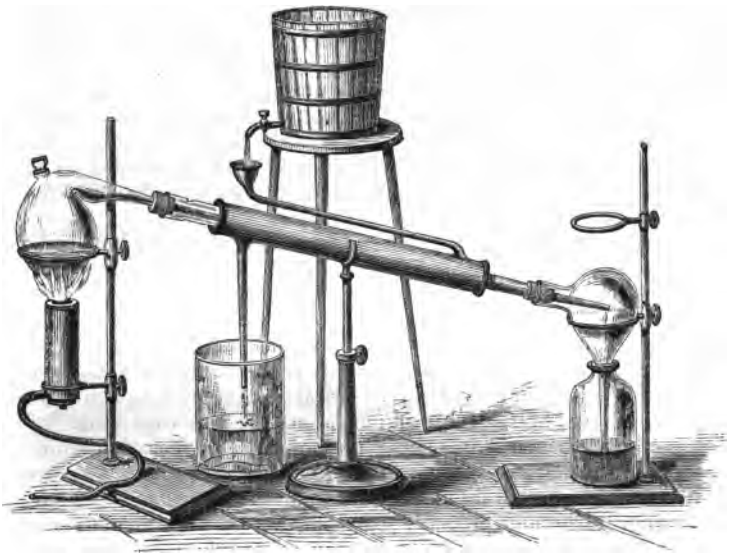

Fig. 31.

vapour, flows out through the vertical tube underneath the upper part of the cylinder: the whole apparatus is thus kept constantly cool, and the distillation proceeds in a uniform and steady manner. The operation is represented in Fig. 31.

It is sometimes required to conduct the gaseous products of distillation into vessels containing water or other liquids, as in the preparation of hydrochloric and sulphurous acids, solution of ammonia, etc.; for such occasions the apparatus of Liebig would obviously be unfitted, and the arrangement represented in Fig. 32 is best adapted to the purpose. It consists of a

series of vessels placed side by side, and connected by tubes in such a manner that the tube originating in one vessel descends nearly to the bottom of the vessel following it. A simple inspection of the figure will show the direction in which the current is supposed to be passing. After having acted on the water or solution in the first bottle, it passes through the bent tube into the second, and thence into the third. The junctions of the tubes with the bottles are made in various ways: sometimes they pass through corks as in the figure, at other times

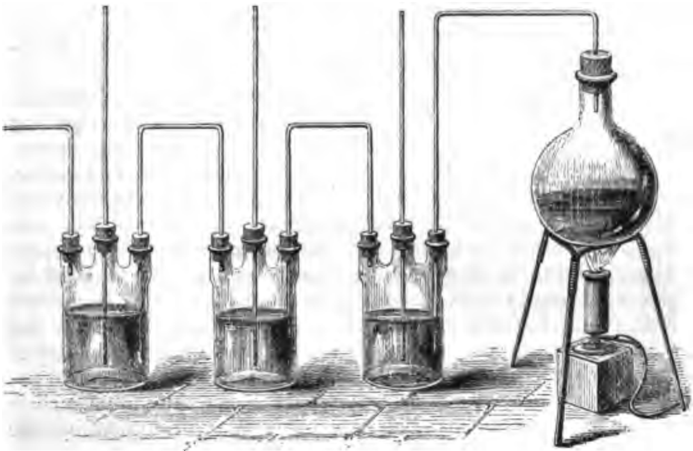

Fig. 32.

they are made tight by glazier's putty, or linseed paste, or plaster of Paris. To prevent stiffness and rigidity, the tubes leading from bottle to bottle may be made of separate pieces united together tight by tubes or collars of caoutchouc. This arrangement has received the name of 'Woulfe's apparatus,' but it was first devised by Glauber. The upright tubes in the centre of each bottle are safety tubes, and are intended to admit air, when from any cause the pressure within is so far diminished as to be considerably less than that of the atmosphere.

It is sometimes required to collect for examination the uncondensable elastic fluids evolved during distillation, besides the liquid results; the object in such cases is readily attained

by bending the delivering-tube of the third bottle into a curve, and bringing it under the shelf of the hydro-pneumatic or the mercurio-pneumatic trough; when the operation is conducted on a small scale, the receiver may be made out of a piece of tube, bent in the manner represented in Fig. 33; the distillation is conducted precisely in the same manner as with an ordinary retort and receiver.

The apparatus required for sublimation may be tubes, flasks, retorts, capsules, or crucibles. When no great heat is required, as with *camphor*, *naphthaline*, *iodine*, etc., the alembic may be used with advantage. For substances requiring a higher temperature, such as *calomel*, *cinnabar*, etc., Florence flasks, bedded and heated in sand and provided with bent tubes, tightly luted, for conveying the volatile products into other flasks for condensation, are exceedingly useful. Many substances may be conveniently and simply purified by placing them in a dish or pan, the mouth of which is covered with coarse filtering-paper perforated with holes, and over the whole a cap or cone of stiff paper, secured round the rim of the pan by twine or paste; heat is then applied to the dish, the volatile substance rises and condenses upon the inner surface of the cap, its mechanical impurities being retained by the filtering-paper.

Fig. 33.

CHAPTER II.

ON REAGENTS.

25. THOSE substances which are employed by the chemist to give him information as to the nature of the subject of his examinations, have received the general name of *Reagents;* though the manner in which they act, and the phenomena to which they give rise, are exceedingly varied. These bodies are of the highest importance to the analyst; indeed the judicious use of them, and the correct interpretation of the appearances presented by their action, constitute the skill of the analytical chemist. We shall here describe the preparation and uses of the most important of these substances, without, however, making any attempt to classify them.

The reagents to which we shall direct attention are the following:—

1. Blue litmus-paper.
2. Red litmus-paper.
3. Turmeric paper.
4. Georgina paper.
5. Solution of indigo.
6. Starch paste.
7. Lead paper.
8. Sulphuric acid.
9. Nitric acid.
10. Hydrochloric acid.
11. Nitro-muriatic acid (aqua regia).
12. Acetic acid.
13. Oxalic acid.
14. Tartaric acid.
15. Hydrate of Potassa.
16. Carbonate of potassa.
17. Carbonate of soda.
18. Ammonia.
19. Sesquicarbonate of ammonia.
20. Chloride of ammonium.
21. Sulphide of ammonium *(hydrosulphuret of ammonia)*.
22. Sulphide of potassium.
23. Oxalate of ammonia.
24. Hydrosulphuric acid *(sulphuretted hydrogen)*.
25. Ferrocyanide of potassium.
26. Ferridcyanide of potassium

27. Chromate of potassa.
28. Sulphate of potassa.
29. Bisulphate of potassa.
30. Cream of tartar.
31. Cyanide of potassium.
32. Antimoniate of potassa.
33. Caustic baryta (solution).
34. Chloride of barium.
35. Nitrate of baryta.
36. Phosphate of soda.
37. Phosphate of soda and ammonia (microcosmic salt).
38. Nitrate of potassa.
39. Biborate of soda (borax).
40. Nitrate of silver.
41. Ammonio-nitrate of silver.
42. Sulphate of copper.
43. Iodide of potassium.
44. Acetate of lead.
45. Basic acetate of lead.
46. Protosulphate of iron.
47. Lime water.
48. Sulphate of lime.
49. Chloride of calcium.
50. Protochloride of tin.
51. Bichloride of platinum.
52. Sesquichloride of iron.
53. Sulphurous acid.
54. Hydrofluosilicic acid.
55. Chlorine water.
56. Chloride of mercury.
57. Subnitrate of mercury.
58. Molybdate of ammonia.
59. Protonitrate of cobalt.
60. Distilled water.
61. Alcohol.
62. Ether.

(1.) *Litmus Paper.*—This is an exceedingly delicate test of the presence of an acid; it is most conveniently prepared by dipping thin unsized paper into an infusion of the colouring principle in hot water until it acquires a full blue colour. The paper is dried by exposure to the air, and kept carefully protected from the light, which injures and finally destroys the colour. The blue colour of this paper is instantly changed red by contact with a fluid having an acid reaction.

(2.) *Red Litmus Paper.*—This is a valuable test of the presence of an alkali. To prepare it, a few drops of hydrochloric acid are mixed with a large quantity of water, and the blue paper immersed in it until it becomes slightly reddened: it is then removed and dried for use. The blue colour is restored by contact with an alkali.

(3.) *Turmeric Paper.*—This is prepared in the same manner as litmus paper; it should have a fine yellow colour; it indicates the presence of an alkali by changing to a red brown.

(4.) *Georgina Paper.*—This, when properly prepared, is an excellent test of both acids and alkalies; by the former it is coloured red, and by the latter green. It is prepared by dipping paper into the coloured infusion of the petals of the *Georgina purpurea*, and should have a fine violet colour.

(5.) *Solution of Indigo.*—Commercial indigo is digested in

concentrated sulphuric acid, and the solution diluted with water till it is just distinctly blue. It is an excellent test for nitric acid, which, aided by heat, discharges the colour.

(6.) *Starch Paste.*—Common arrowroot starch is rubbed with cold water, and boiling water then added until a thin paste is formed. It is an invaluable test for free iodine; when brought into contact with which, an intense blue compound is formed.

(7.) *Lead Paper.*—Paper is saturated with a strong solution of basic acetate of lead, cut into strips and dried. It forms an extremely delicate test of the presence of sulphuretted hydrogen, which instantly communicates to it a deep brown-black colour.

(8.) *Sulphuric Acid*, HO,SO_3.—The commercial oil of vitriol always contains sulphate of lead, sometimes also nitric acid, arsenic, and tin. The first of these impurities is removed by diluting the acid with water; a turbidity indicates sulphate of lead, which is insoluble in the diluted acid. Nitric acid is indicated by the blue colour of solution of indigo being discharged when boiled with the acid. Arsenic is indicated by passing a stream of sulphuretted hydrogen through the clear diluted acid; a yellow precipitate is formed: if the precipitate be brown, it indicates tin. From all these impurities it may be freed by distillation; the first portions being rejected, and not more than three-fourths of the acid in the retort drawn over; for almost every qualitative operation the commercial acid may be employed. Sulphuric acid is of the most extensive use to the chemist, from its strong affinity for bases. It liberates most other acids from their combinations; and, from its powerful affinity for water, it effects remarkable changes in many substances in which the elements of that fluid exist. It is a powerful oxidizing agent, and in a diluted state it serves as a test for ***barium***, ***strontium***, and ***lead***.

(9.) *Nitric Acid*, HO,NO_5.—This acid, the aqua-fortis of commerce, is prepared by distilling equal weights of oil of vitriol and nitre. It frequently contains sulphuric and hydrochloric acids, from which it may be freed, by adding nitrate of silver as long as a precipitation takes place, and then redistilling. This operation may, however, be avoided, if in the original preparation of the acid the first portions, about one-tenth or one-eighth of the whole, be collected in a separate receiver; these portions will contain all the impurities, and

the remainder will be quite pure. Nitric acid is used as a solvent for metals, sulphides, etc., and as a powerful oxidizing agent.

(10.) *Hydrochloric Acid*, HCl.—The muriatic acid of commerce is not sufficiently pure for analytical purposes. It contains sulphuric acid and iron, sometimes also sulphurous acid, chlorine, and arsenic. It is best prepared by the following process of Gregory:—Six parts by weight of pure common salt are introduced into a flask, and gently heated with a cool mixture of ten parts by weight of oil of vitriol and four parts of water. The gas is conducted into a flask containing a quantity of distilled water, equal in weight to the salt, and surrounded with water in which lumps of ice are floating. The tube delivering the gas must dip about one-eighth of an inch into the water in the bottle; the process takes about two hours, and the acid obtained is quite pure and colourless.

Hydrochloric acid is very extensively used as a solvent, and for the detection of silver, mercury, and lead.

(11.) *Nitro-muriatic Acid, or Aqua Regia.*—This acid is prepared by adding nitric acid to twice or thrice its volume of strong hydrochloric acid; both acids undergo decomposition, hyponitric acid, chlorine, and water being formed. When the liquid is saturated with chlorine, this mutual decomposition ceases; but it recommences on the removal of the chlorine either by heat or by its combination with some other substance. Aqua regia is consequently the most powerful of solvents: its principal use in analytical chemistry is for dissolving gold and platinum, and for decomposing certain metallic sulphides.

(12.) *Acetic Acid*, $HO,C_4H_3O_3$.—The acetic acid of commerce frequently contains traces of sulphuric acid, but it may be obtained sufficiently pure for most analytical operations. If required quite free from all impurities, it is most conveniently prepared by distilling a mixture of ten parts of neutral acetate of lead with three of sulphate of soda, in a retort, with a cooled mixture of two and a half parts of sulphuric acid, and an equal weight of water: the distillation is continued to dryness. The acid thus obtained leaves no residue on evaporation. Acetic acid is employed as a solvent, and for acidifying liquids in the place of the mineral acids.

(13.) *Oxalic Acid*, HO,C_2O_3.—The commercial acid is purified by two or three recrystallizations. It should leave no residue on ignition. It is employed as a precipitant of certain

substances, particularly calcium, for the detection of which it is a very valuable reagent. All the oxalates are soluble in the stronger acids.

(14.) *Tartaric Acid*, $2HO, C_4H_8O_{10}$.—The commercial acid is sufficiently pure: well-defined crystals should be selected. It should be kept in powder, as its solution decomposes by keeping. It is employed to prevent the precipitation of certain metallic oxides by alkalies, and as a test for potassium.

(14.) *Hydrate of Potassa*, KO, HO.—The best method of preparing this valuable reagent is to dissolve two parts of pure carbonate of potassa in twenty parts of boiling water in an iron pot, and to add in small portions at a time, to the boiling liquid, cream of lime (made by slaking one part of quicklime with boiling water); after boiling a few minutes, the vessel is covered and allowed to stand for twenty-four hours; the clear liquid is then decanted. To obtain the potassa in the solid state, the liquid is evaporated to an oily consistence in a silver basin, poured out on a silver dish, and allowed to cool; it is then broken into fragments and preserved in well-stoppered bottles. Schubert recommends the following simple method of preparing a solution of pure potash:—Add a hot solution of *hydrate of baryta* to a solution of *sulphate of potassa* until the liquid gives no further precipitate either with baryta or with sulphate of potassa.

The uses of potassa in analytical chemistry are very numerous;—as a precipitant; as a solvent; as a means of separating certain oxides from others; and as a test for ammonia, which, aided by heat, it expels from all its salts.

(16.) *Carbonate of Potassa*, KO, CO_2.—This salt is best prepared by calcining pure cream of tartar: the incinerated mass is boiled in distilled water, filtered, and the clear liquid evaporated to dryness in a clean iron vessel, with constant stirring towards the end of the process; the dried mass must be kept in a well-stoppered bottle, and one part dissolved in five or six of distilled water for use. The carbonate of potassa of commerce usually contains alkaline sulphates and chlorides; alumina and silica. Carbonate of potassa is extensively employed as a precipitant, and for the decomposition of many insoluble salts, particularly organic, with metallic bases.

(17.) *Carbonate of Soda*, NaO, CO_2.—This salt is obtained pure by heating the best bicarbonate of soda of commerce for some time to low redness: its uses are the same as those of

carbonate of potassa. It is an indispensable reagent in blowpipe operations;—as a flux; as a solvent; and as a decomposing agent. Its solution should not be discoloured by sulphide of ammonium, when neutralized with hydrochloric acid it should give no turbidity with chloride of barium, and when evaporated to dryness with hydrochloric acid the residue should dissolve completely in water.

(18.) *Ammonia*, NH_3.—Sal-ammoniac is mixed with an equal weight of slaked lime, a little water added, and the mixture heated in a stoppered retort. The disengaged gas is first allowed to pass through a small quantity of water in a wash-bottle, and from thence into another bottle nearly filled with distilled water immersed in a vessel containing ice-cold water; this bottle, for better security against sudden absorption, may be furnished with a safety tube. The water will absorb 670 times its bulk of the gas, and become possessed of all its chemical properties in a very high degree. It should be kept in small well-stoppered bottles, and not in one large one, as every time it is exposed to the air it absorbs a certain quantity of carbonic acid, its freedom from which is proved by its not rendering lime-water turbid. Ammonia is in constant use for neutralizing acids, its peculiar fitness for which consists in its not introducing any fixed matter; for precipitating insoluble bases; and for separating them from each other. The ammonia of commerce is generally pure. It should give no turbidity with chloride of calcium, or with oxalate of ammonia, nor with nitrate of silver, when neutralized with nitric acid, and when evaporated should leave no residue.

(19.) *Sesquicarbonate of Ammonia*, $2NH_4O,3CO_2$.—The sesquicarbonate of ammonia of commerce is dissolved in four parts of distilled water, and one of liquor of ammonia added. The solution when evaporated should leave no residue. This reagent is employed as a precipitant, and is very useful as a substitute for carbonate of potass, in cases where the introduction of a fixed base would be inconvenient. It is of special use in the separation of *calcium*, *barium*, and *strontium* from *magnesium*, the latter not being precipitated in the presence of ammoniacal salts.

(20.) *Chloride of Ammonium*, NH_4Cl.—Sal-ammoniac of commerce is purified by two or three recrystallizations. Its solution in water should be neutral, and hydrosulphuret of ammonia should not discolour it: it should volatilize entirely

when heated on platinum foil. The salt should be dissolved for use in eight parts of distilled water. It is of great use in analysis as a precipitant of various substances soluble in potassa, but insoluble in ammonia, and for keeping in solution certain oxides or salts when others are precipitated by ammonia or other reagents.

(21.) *Sulphide of Ammonium*, NH_4S *(Hydrosulphuret of Ammonia)*.—This reagent is prepared by transmitting sulphuretted hydrogen gas through solution of ammonia, till the liquid gives no precipitate with sulphate of magnesia. It must be kept in well-stoppered bottles free from lead. When first prepared, it contains excess of sulphuretted hydrogen, is nearly colourless, and does not give a precipitate of sulphur when mixed with an acid; but by exposure to the air it gradually absorbs oxygen, and assumes a yellow tint from the presence of excess of sulphur, of which element it now yields a precipitate on the addition of an acid. It is necessary to bear in mind these facts. Sulphide of ammonium is of great use for subdividing into two groups those metals which are precipitated as sulphides by sulphuretted hydrogen, from their acid solutions; some of these sulphides being soluble, others insoluble in sulphide of ammonium. It also subdivides into groups those metals that are not precipitated by sulphuretted hydrogen from their acid solutions; some of these metals being precipitated by sulphide of ammonium, while others remain in solution: it likewise precipitates certain oxides as hydrates by the action of its ammonia alone, and certain salts that are dissolved only in free acids.

(22.) *Sulphide of Potassium*, KS_5.—This reagent is easily prepared by transmitting a stream of sulphuretted hydrogen through a solution of caustic potassa as long as the gas is absorbed, and then mixing the saturated solution with an equal volume of the same caustic potassa.

(23.) *Oxalate of Ammonia*, NH_4O, C_2O_3.—This reagent is prepared by slightly supersaturating a solution of pure oxalic acid with carbonate of ammonia, and crystallizing: one part of the salt is dissolved in twenty or twenty-four parts of water for use; it is employed for the detection and precipitation of lime, and is more convenient than oxalic acid, as its solution does not decompose by keeping.

(24.) *Hydrosulphuric Acid*, HS *(Sulphuretted Hydrogen)*.—Fragments of *protosulphide of iron* are covered with water in a

The condenser is a hollow metal cylinder, through the centre of which a glass tube passes, being fixed water-tight by means of perforated corks covered with cement. This tube is connected either by a cork or by tubing with the beak of a retort; a constant stream of water is caused to flow from the reservoir placed above, down the funnel, thus entering the cylinder at its lower part. The water, warmed by the condensation of the

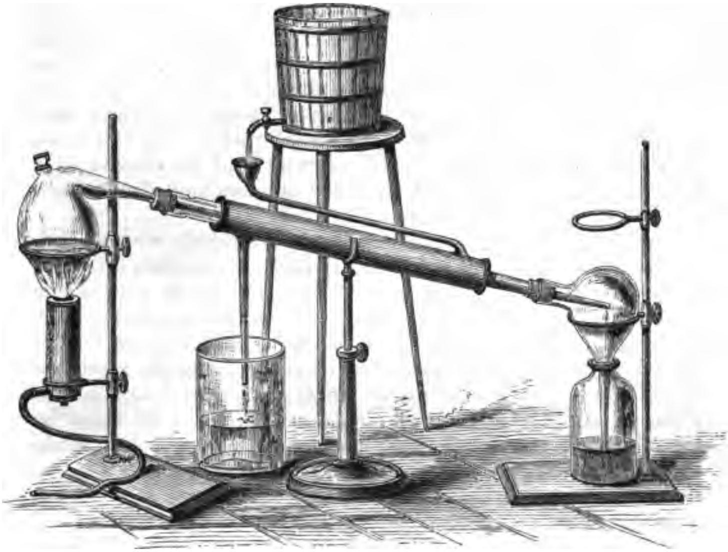

Fig. 31.

vapour, flows out through the vertical tube underneath the upper part of the cylinder: the whole apparatus is thus kept constantly cool, and the distillation proceeds in a uniform and steady manner. The operation is represented in Fig. 31.

It is sometimes required to conduct the gaseous products of distillation into vessels containing water or other liquids, as in the preparation of hydrochloric and sulphurous acids, solution of ammonia, etc.; for such occasions the apparatus of Liebig would obviously be unfitted, and the arrangement represented in Fig. 32 is best adapted to the purpose. It consists of a

series of vessels placed side by side, and connected by tubes in such a manner that the tube originating in one vessel descends nearly to the bottom of the vessel following it. A simple inspection of the figure will show the direction in which the current is supposed to be passing. After having acted on the water or solution in the first bottle, it passes through the bent tube into the second, and thence into the third. The junctions of the tubes with the bottles are made in various ways: sometimes they pass through corks as in the figure, at other times

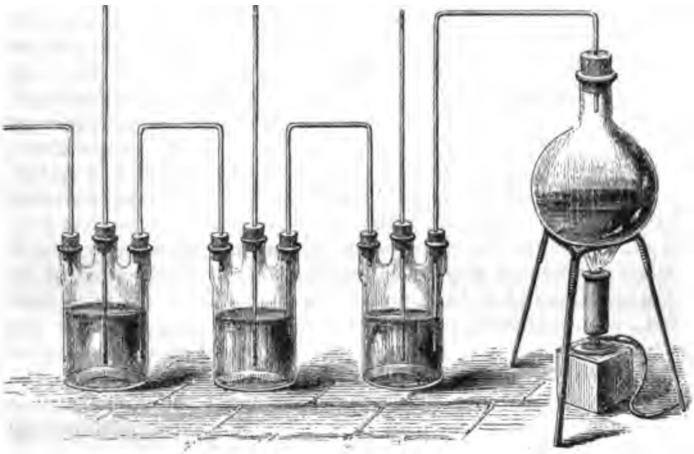

Fig. 32.

they are made tight by glazier's putty, or linseed paste, or plaster of Paris. To prevent stiffness and rigidity, the tubes leading from bottle to bottle may be made of separate pieces united together tight by tubes or collars of caoutchouc. This arrangement has received the name of 'Woulfe's apparatus,' but it was first devised by Glauber. The upright tubes in the centre of each bottle are safety tubes, and are intended to admit air, when from any cause the pressure within is so far diminished as to be considerably less than that of the atmosphere.

It is sometimes required to collect for examination the uncondensable elastic fluids evolved during distillation, besides the liquid results; the object in such cases is readily attained

acid, consisting of one part of oil of vitriol mixed with six or eight parts of water, is to be poured into the uppermost globe, from which it passes down into the lowermost globe, and thence up into the middle globe, the stopcock being opened to let out the atmospheric air. Hydrosulphuric acid gas is immediately generated, and as much of it is allowed to escape as serves to sweep the atmospheric air completely out of the apparatus. The stopcock is then closed, and the apparatus is ready for use. The *quantity* of gas delivered depends upon the arrangement of the stopcock. It can be delivered in single bubbles slowly, or in a rapid current. The delivery pipe is made short or long, according to the depth of liquor into which it is to pass. It must of

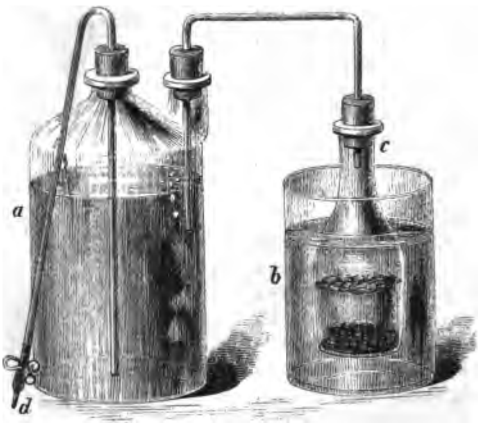

Fig. 36.

course be changed for every experiment. The siphon at the top of the apparatus must contain so much water as to allow atmospheric air to pass either way into or out of the apparatus, according as the stopcock is open or closed. If any sulphide of iron falls into the globe *b*, it makes a constant disengagement of gas, which, if not observed, may drive so much acid up into the uppermost globe as to cause an overflow to take place. It is proper, therefore, that this apparatus should always stand in a stoneware pan, to catch any acid that may overflow. When the apparatus requires cleaning or the sulphide of iron needs

washing, the acid can be poured off through the stoppered neck in the lowest globe.

In Fig. 36 is represented Mohr's apparatus for a constant supply of a saturated solution of sulphuretted hydrogen.* It not only serves to prepare a solution of the gas without contact with atmospheric air, but to preserve it in that condition, and yet to afford a supply of the solution either in drops or in quantity, readily and conveniently. The Woulff's bottle, *a*, is filled with air-free distilled water; *b c* is an apparatus for preparing hydrosulphuric acid gas; the jar *b* contains dilute sulphuric acid; the flask *c* contains lumps of sulphide of iron. The bottom of the flask is cut out, and replaced by a perforated plate of lead, upon which the sulphide of iron rests at about three-quarters of an inch from the cut bottom-edge of the flask. To set this apparatus in action, the vessels *a*, *b*, and *c*, having received their respective charges, the cork which fixes the siphon *d* in the bottle *a* is loosened, and the apparatus being then placed together, the gas is produced, and gradually drives out the atmospheric air from the vessels *c* and *a*. The siphon cork is then fixed, and sulphuretted hydrogen gas is produced in *c* and absorbed by the water in *a*, until the latter is saturated. The acid then descends from the flask *c* into the jar *b*, and the operation stops. The siphon *d* is terminated outside by a glass delivery-tube attached by a caoutchouc connector and a pinchcock. Whenever the sulphuretted hydrogen water is required, the pinchcock is opened, a little liquor run off to waste to clean the end of the delivery tube, and then as much liquor is run out as the experiment requires. To supply the vacuum thus produced in the bottle *a*, the atmospheric air pressing upon the liquor in the jar *b*, drives it up into the flask *c*, and causes the production of as much hydrosulphuric acid gas as is required to make up the quantity run off by the siphon *d*. When the liquor of the bottle *d* is exhausted, a fresh supply of cold air-free distilled water is put into the bottle by the siphon neck, and the process of saturation goes on afresh. The corks of this apparatus should be coated with a mixture of fat and wax, to make them air-tight.

(25.) *Ferrocyanide of Potassium*, K_2FeCy_3; *or* K_2Cfy.—The commercial yellow prussiate of potassa is sufficiently pure for analytical purposes; one part is dissolved for use in ten or

* Mohr's 'Commentar zur Preussischen Pharmacopœia,' and Griffin's 'Chemical Recreations.'

twelve parts of water. It is of especial use for the detection of *sesquioxide of iron* and *oxide of copper*.

(26.) *Ferridcyanide of Potassium*, $K_3Fe_2Cy_6$; *or* K_3Cfdy.—This reagent is prepared by transmitting a stream of chlorine gas through a solution of the above salt until it ceases to produce a blue precipitate, with a solution of sesquichloride of iron. Its crystals have a magnificent red colour; to procure them, the solution is concentrated by evaporation, and rendered feebly alkaline by carbonate of potassa. This reagent serves to detect *protoxide of iron* by the formation of a characteristic blue precipitate.

(27.) *Chromate of Potassa*, KO,CrO_3.—Bichromate of potash of commerce is dissolved in water, and carbonate of potash added till the solution reacts slightly alkaline; from the concentrated liquid yellow crystals may be obtained. It is employed principally as a test for *lead*, with which it forms a pigment known as chrome yellow.

(28.) *Sulphate of Potassa*, KO,SO_3.—The salt of commerce is purified by two or three crystallizations, and dissolved for use in ten or twelve parts of water; it is used for the detection and separation of *strontium* and *barium*.

(29.) *Bisulphate of Potassa*, KO,SO_3; HO,SO_3.—This is the fusible salt remaining when nitrate of potash is decomposed by two equivalents of oil of vitriol in the process for making nitric acid; it is extensively employed in blowpipe operations; in solution it indicates lithium, boracic acid, nitric acid, hydrofluoric acid, bromine, and iodine, and separates oxides of *barium* and *strontium* from other earths and metallic oxides.

(30.) *Bitartrate of Potassa*, $KO,HO,C_8H_4O_{10}$; *or* $KO, HO,\overline{T}$.—The cream of tartar of commerce is sufficiently pure; it is useful in certain cases for separating metals from each other.

(31.) *Cyanide of Potassium*, KCy.—Eight parts of roasted ferrocyanide of potassium are fused at a bright red-heat in a covered crucible with three parts of dry carbonate of potassa; the fused mass is poured carefully into a warm dish, and when cold, broken into fragments, and kept in a well-closed bottle: it must not be kept in solution, but dissolved as required in four or five parts of water. In analysis, its most important application is as a means of separating *cobalt* from *nickel*. As a blowpipe reagent mixed with an equal weight of carbonate of soda, it is exceedingly valuable from its powerful reducing

action; and from its easy fusibility it is of special application in the reduction of *arsenic*.

(32.) *Bimetantimoniate of Potassa*, $2KO,SbO_5$.—A mixture of one part of crude antimony with four parts of powdered nitre is thrown, a little at a time, into a crucible at a dull red-heat; the mass is kept in a pasty state, with occasional stirring, for about half an hour, after which it is cooled, well washed, and heated to bright redness for half an hour, with two-thirds of its weight of pure carbonate of potassa. The cooled mass is digested with about fifty parts of warm water, and filtered for use when cold. It should not contain excess of alkali. Its use is as a test for soda, with which, provided no other base be present, it forms a very sparingly soluble crystalline precipitate.

(33.) *Caustic Baryta*, BaO,HO.—Sulphide of barium is boiled with excess of oxide of copper or oxide of lead, and filtered when the liquid gives a white precipitate, with acetate of lead: it is then diluted with water, and preserved in well-closed bottles. Its most important use is as a precipitant of *magnesia*.

(34.) *Chloride of Barium*, $BaCl$.—To prepare this useful reagent, six parts of heavy spar (sulphate of baryta) are exposed to an intense red-heat, with a mixture of one part of powdered charcoal and one and a half of fluor spar; the resulting sulphide of barium is boiled with slight excess of hydrochloric acid, filtered, and crystallized two or three times. The solution of these crystals must be neutral to test-papers, not affected by sulphuretted hydrogen or sulphide of ammonium: it must, moreover, leave no residue when mixed with excess of sulphuric acid, filtered and evaporated. Its most important use is as a means of detecting and estimating *sulphuric acid*. From the property which baryta possesses of forming soluble salts with some acids, and insoluble salts with others, it is likewise a valuable reagent for distinguishing one group of acids from another.

(35.) *Nitrate of Baryta*, BaO,NO_5.—Native carbonate of baryta is digested with dilute nitric acid, the solution filtered and crystallized two or three times. Its uses and applications are the same as those of chloride of barium.

(36.) *Phosphate of Soda*, $2NaO,HO,PO_5$.—The commercial salt is crystallized and dissolved for use in ten or twelve parts of water. It serves as a test for alkaline earths in general, but

especially for the detection and estimation of *magnesia*, which it precipitates with the addition of ammonia as the basic phosphate of ammonia and magnesia.

(37.) *Phosphate of Soda and Ammonia*, NaO,NH_4O,PO_5.—This salt (microcosmic salt) is prepared by boiling one hundred parts of crystallized phosphate of soda with sixteen of sal-ammoniac. Chloride of sodium separates, and the liquid, when filtered and evaporated, yields the double salt in fine crystals. When this salt is heated on charcoal or platinum wire, it loses water and ammonia, metaphosphate of soda being formed, which has the power of fusing a great number of chemical compounds. Hence its great use as a blowpipe reagent.

(38.) *Nitrate of Potassa*, KO,NO_5.—The nitre of commerce is purified by repeated crystallizations; its solution should give no precipitate with nitrate of silver, or chloride of barium: it is extensively employed as an oxidizing agent.

(39.) *Biborate of Soda*, $NaO,2BO_3$.—The borax of commerce is purified by recrystallization. It should be exposed to a gentle heat in a platinum crucible till it no longer swells up; it is then powdered and kept for use. When heated on the ring of platinum wire, it should give a clear transparent glass. This glass possesses the property of dissolving most metallic oxides, the smallest portions of which communicate to it a colour; hence its important use as a blowpipe reagent.

(40.) *Nitrate of Silver*, AgO,NO_5.—Standard silver is dissolved in nitric acid, evaporated to dryness, and heated till all the copper present is converted into black oxide, which may be known by dissolving a portion of the fused salt in water and adding ammonia, which should not make the solution blue. The fused mass is dissolved in water, filtered and crystallized; the crystals are dissolved for use in fifteen or twenty parts of distilled water. It may be known to be pure by the filtrate from the precipitate, which it forms with excess of hydrochloric acid, leaving no residue when evaporated on a watch-glass. It is employed for arranging acids into groups, and is of special application in testing for, and estimating *hydrochloric acid*.

(41.) *Ammonio-Nitrate of Silver*.—Ammonia is dropped into solution of nitrate of silver till the precipitate which first forms is nearly redissolved. It is employed for the detection of *arsenic*.

(42.) *Sulphate of Copper*, CuO, SO_3.—Blue vitriol is purified

by two or three crystallizations. A solution of one part of this salt mixed with two and a quarter parts of protosulphate of iron, is employed for the precipitation of *hydriodic acid*, as protiodide of copper. Ammonio-sulphate of copper, prepared in the same manner as the corresponding silver salt, is also employed as a test for *arsenic*.

(43.) *Iodide of Potassium*, KI.—The commercial salt is tested for carbonate of potassa by treating it with hot alcohol, in which the latter salt is insoluble. It is a reagent for certain metals, particularly for *lead* and *mercury*, with which it forms characteristic precipitates.

(44.) *Neutral Acetate of Lead*, $PbO,C_4H_3O_3$.—The best sugar of lead of commerce is dissolved in ten or twelve parts of distilled water; it is useful for arranging acids into groups, and for the special detection of *chromic acid*.

(45.) *Basic Acetate of Lead*, $3\,PbO,C_4H_3O_3$.—Seven parts of well-washed litharge and six of the best neutral acetate of lead are gently heated and agitated with thirty parts of water till the sediment has become perfectly white; the liquid is then decanted and preserved for use in a well-closed bottle. It has the same applications as the last-described salt, but its chief use is as a test for *sulphuretted hydrogen*.

(46.) *Protosulphate of Iron*, FeO,SO_3.—Clean iron nails are digested with dilute sulphuric acid till hydrogen ceases to be evolved. The solution is filtered, and the crystals obtained washed with water slightly acidified with sulphuric acid and dried. This salt is a powerful deoxidizing agent, and is of especial application as a test for *nitric acid*. It also precipitates *gold* in the metallic state, and forms a blue compound with ferridcyanide of potassium.

(47.) *Lime Water*, CaO,HO.—Fresh slaked lime is agitated with cold water, allowed to settle, and the clear fluid preserved in well-stopped bottles. It serves to detect *carbonic acid*, and as a means of distinguishing certain organic acids.

(48.) *Sulphate of Lime*, CaO,SO_3.—The precipitate formed on adding chloride of calcium to dilute sulphuric acid is well washed, digested, and agitated with water, and the fluid filtered for use. It is employed to distinguish between *calcium*, *strontium*, *and barium*.

(49.) *Chloride of Calcium*, $CaCl$.—Pure carbonate of lime is dissolved in dilute hydrochloric acid, the solution evaporated to perfect dryness, and the residue redissolved in distilled

water. It must be perfectly neutral. It is of great use for the classification of organic acids.

(50.) *Protochloride of Tin*, $SnCl$.—Granulated tin is boiled with concentrated hydrochloric acid, the metal being in excess; it is then diluted with four or five times its quantity of water, slightly acidulated with hydrochloric acid, and filtered. It must be kept in well-closed bottles containing fragments of metallic tin to prevent the protochloride from passing into the state of perchloride. It is a powerful reducing agent. It also serves to detect *mercury*, and, when mixed with nitric acid, it indicates the presence of *gold*.

(51.) *Bichloride of Platinum*, $PtCl_2$.—The solution of the metal in aqua regia is evaporated to dryness on the water-bath, and redissolved in eight or ten parts of water. It is of great use in analytical chemistry for the detection and estimation of *potassium* and *ammonium*.

(52.) *Sesquichloride of Iron*, Fe_2Cl_3.—Clean iron nails are digested with diluted hydrochloric acid; the decanted acid liquid is then boiled with successive additions of nitric acid, in a capacious vessel, till all effervescence ceases, and till it no longer tinges solution of ferridcyanide of potassium blue; it is then precipitated with excess of ammonia, and the well-washed hydrated peroxide of iron is heated with hydrochloric acid, care being taken that it is not all dissolved, it being necessary that the test should not contain excess of acid; it is then filtered for use. It is employed as a means of classifying organic acids, and is also of great use in the analysis of the phosphates of the alkaline earths.

(53.) *Sulphurous Acid*, SO_2.—This is prepared by transmitting the gases produced by the action of six parts of oil of vitriol on one part of charcoal (carbonic and sulphurous acid gases) through ice-cold water till no more is absorbed. It must be kept in well-closed bottles, and should always smell strongly of the acid. It is a powerful means of reduction; it precipitates mercury from its solution, converts chromic acid into oxide of chromium, arsenic acid into arsenious acid, etc.

(54.) *Hydrofluosilicic Acid*, HF,SiF_2.—Equal weights of a mixture of powdered fluor spar and quartz are gently heated, in a retort, with oil of vitriol, and the gas evolved passed into water, the extremity of the delivering tube dipping into mercury placed at the bottom of the jar, in order to prevent the tube from becoming choked up with the silicic acid which is

precipitated the instant the gas comes into contact with water. The gelatinous mass is filtered through linen, and the filtrate preserved for use. Hydrofluosilicic acid forms an insoluble compound with *potassium*, which it is sometimes employed to separate from chloric acid. It is also used to discriminate between *barium* and *strontium*, with the former of which it forms a crystalline precipitate.

(55.) *Chlorine Water.*—The gas evolved by heating finely-powdered peroxide of manganese with five or six times its weight of hydrochloric acid is conducted into cold water, until the fluid is saturated. It must be kept in a well-closed bottle and preserved from the light. It is employed to expel *iodine* and *bromine* from their combinations.

(56.) *Chloride of Mercury*, $HgCl$.—The corrosive sublimate of commerce is purified by crystallization, and dissolved for use in twelve or fourteen parts of water. It forms characteristic coloured precipitates with certain acids.

(57.) *Subnitrate of Mercury*, Hg_2O,NO_5.—One ounce of pure nitric acid is poured on one ounce of mercury and allowed to remain for twenty-four hours in the cold; the crystals formed are dissolved in water acidified by nitric acid, and filtered. A small quantity of metallic mercury should be put into the bottle in which this reagent is preserved.

(58.) *Molybdate of Ammonia.*—This reagent, which is used as a test for phosphoric acid, is prepared by roasting sulphide of molybdenum until it ceases to liberate sulphurous acid, and becomes completely converted into molybdic acid, which while hot is yellow, but white when cold. It is digested with ammonia, filtered, and then mixed with hydrochloric acid in quantity sufficient to redissolve the precipitate which at first forms. The solution should be perfectly colourless; if it has a yellow tinge, it indicates the presence of *phosphoric acid.*

(59.) *Protonitrate of Cobalt*, CoO,NO_5.—It is not easy to obtain this reagent quite pure, though for blowpipe experiments it is a matter of great consequence that it should be so. Fresenius gives the following directions for preparing it:—an intimate mixture of two parts of very finely-powdered cobalt, four parts of saltpetre, one part of effloresced carbonate of soda, and one part of dry carbonate of potassa, is projected in small portions into a red-hot crucible, which is then exposed to the strongest possible heat till the mass is fusing; when cold it is reduced to powder, boiled with water, and the well-washed

mass dissolved in hydrochloric acid; the gelatinous mass is carefully evaporated to dryness; the residue boiled with water, filtered, and carbonate of ammonia (carbonate of potassa is better) added to the filtrate while kept at the boiling heat till all acid reaction ceases; the filtered solution is precipitated by carbonate of potassa, and the precipitate obtained washed and dissolved in nitric acid. The solution is evaporated to dryness at a gentle heat, and one part of the residue dissolved in ten parts of water for use. Solution of nitrate of cobalt is employed to distinguish certain metals in the oxidating flame of the blowpipe. Thus, *alumina* acquires a beautiful pale blue colour, *magnesia* a rose-red tint, and oxide of *zinc* a bright green. A few drops of the solution are placed on the substance to be operated upon by means of a platinum wire or dropping tube.

(60.) *Distilled Water.*—No other water should be employed in the laboratory. It should give no precipitate or even turbidity with chloride of barium, nitrate of silver, oxalate of ammonia, or lime water, and should leave no residue on evaporation.

(61.) *Alcohol,* $C_4H_6O_2$.—Rectified spirits of wine, sp. gr. about ·840, are sufficiently strong for most purposes. What is termed absolute alcohol, and which is sometimes required, is prepared by adding carbonate of potassa, that has recently been exposed to a red-heat, to ordinary alcohol until it ceases to dissolve any more; the whole is allowed to digest for twenty-four hours; the liquid is then poured off, mixed with a sufficient quantity of quicklime to absorb the whole, and slowly distilled from a retort on a water bath at the temperature of about 180°; it is then obtained of a sp. gr. of ·7947. It must not redden blue litmus-paper, and must volatilize without leaving any residue.

(62.) *Ether,* C_4H_5O.—Sulphuric ether of commerce is sufficiently strong and pure for all purposes. In inorganic analysis it is employed to detect and isolate *bromine.*

The student is recommended to assure himself by careful testing of the purity of his reagents; by so doing he may not only save himself from much subsequent embarrassment, but he will be gaining much valuable experience in qualitative examinations.

CHAPTER III.

ON THE COMPORTMENT OF THE PRINCIPAL METALLIC OXIDES WITH REAGENTS.

26. By means of certain reagents this extensive class of compounds may be arranged into a series of Groups; some of which, again, by other reagents, may be subdivided into Sections, the whole forming a very convenient classification:—

Group I.—*Metallic oxides not precipitated from their solutions by hydrosulphuric acid, by sulphide of ammonium, or by alkaline carbonates.*

The Alkalies proper, viz. oxide of potassium (potassa), oxide of sodium (soda), oxide of lithium (lithia), and oxide of ammonium (ammonia).

Group II.—*Metallic oxides not precipitated from their solutions by hydrosulphuric acid, but precipitated under certain circumstances, as salts, by sulphide of ammonium, and precipitated by the alkaline carbonates as carbonates.*

The Alkaline Earths, viz. oxide of barium (baryta), oxide of strontium (strontia), oxide of calcium (lime), and oxide of magnesium (magnesia).*

Group III.—*Metallic oxides not precipitated by hydrosulphuric acid, but precipitated, as oxides, by sulphide of ammonium.*

Oxides of aluminum, glucinum, chromium, thorinum, yttrium, cerium, zirconium, titanium, and tantalum.

Group IV.—*Metallic oxides not precipitated from their acid*

* *Oxide of magnesium* is not precipitated by alkaline carbonates in the presence of ammoniacal salts; but it is thrown down under these circumstances by phosphate of soda.

solutions by hydrosulphuric acid, but precipitated, as sulphides, by sulphide of ammonium:

Oxides of zinc, nickel, cobalt, and iron, protoxide of manganese, and sesquioxide of uranium.

Group V.

Section A.—*Metallic oxides precipitated from their solutions, whether acid, alkaline, or neutral, by hydrosulphuric acid.*

Oxides of lead, silver, mercury, bismuth, cadmium, copper, palladium, rhodium, and osmium.

This section may be further divided into two subsections by the comportment of its members with hydrochloric acid; *oxide of silver*, and *suboxide of mercury*, being *completely*, and *oxide of lead partially*, precipitated by that reagent.

Section B.—*Metallic oxides precipitated from their acid solutions by hydrosulphuric acid, but not precipitated by that reagent from their alkaline solutions, their sulphides being soluble in alkaline sulphides.*

Oxides of antimony, arsenic, tin, platinum, iridium, gold, selenium, tellurium, tungsten, vanadium, and molybdenum.

A synoptical view of the comportment of the principal metallic oxides with the general reagents, and the colours of the precipitates occasioned thereby, is given in the following Table.

ANALYTICAL CLASSIFICATION OF THE METALLIC OXIDES.

Group I.	Group II.		Group III.	Group IV.	Group V.		
Metallic oxides not precipitated by hydrosulphuric acid, sulphide of ammonium, or alkaline carbonates.	Metallic oxides not precipitated by hydrosulphuric acid, or by sulphide of ammonium, but precipitated as carbonates by alkaline carbonates.		Metallic oxides not precipitated from their solutions by hydrosulphuric acid, but precipitated as oxides by sulphide of ammonium.	Metallic oxides not precipitated from their acid solutions by hydrosulphuric acid, but precipitated as sulphides by sulphide of ammonium.	Section A. Metallic oxides precipitated from their solutions, whether acid, alkaline, or neutral, by hydrosulphuric acid.	Section B. Metallic oxides precipitated from their acid solutions by hydrosulphuric acid, but not precipitated by that reagent from their alkaline solutions.	Section C. Metallic oxides precipitated from their solutions, either completely or partially, by hydrochloric acid.
Oxides of *Potassium*, *Sodium*, *Lithium*, *Ammonium*, detected by special tests.	*Oxides of* *Barium*, *Strontium*, *Calcium*, (all *white*).	Not precipitated in the presence of ammoniacal salts by alkaline carbonates, but precipitated as phosphate (*white*) by phosphate of soda. *Oxide of Magnesium*	*Oxides of* *Aluminum*, *Glucinum*, *Thorinum*, *Yttrium*, *Cerium*, *Zirconium*, *Tantalum*, *Titanium*, } colourless and voluminous. *Chromium*, bluish-green.	*Oxides of* *Zinc*, white. *Nickel*, *Cobalt*, *Iron*, *Uranium*, } black. *Manganese* (if pure, flesh-coloured).	*Oxides of* *Lead*, *Silver*, *Mercury*, *Bismuth*, *Copper*, *Palladium*, *Rhodium*, } black. *Osmium*, brownish-black. *Cadmium*, yellow.	*Oxides of* *Platinum*, *Iridium*, *Gold*, *Tellurium*, *Tin* (protoxide) } black, or brownish-black. *Antimony*, orange-yellow. *Arsenic*, *Tin* (peroxide), } yellow. *Molybdenum*, *Selenium*, *Tungsten*, } brown yellow.	Completely precipitated. *Mercury* (suboxide), *Silver* (oxide), } white. Partially precipitated. *Lead* (oxide), } white.

GROUP I.

The Alkalies proper: Potassa, Soda, Lithia, and Ammonia.

27. POTASSA. (KO.)

General characters of Hydrate of Potassa (KO,HO).—When pure, it is quite white, dissolving in water with the disengagement of heat, and attracting both water and carbonic acid from the atmosphere. It is highly caustic and eminently alkaline. Nearly all its salts being soluble in water, it is capable of being precipitated by a very few reagents. Its presence is however evinced by the following.

(Solution of Chloride of Potassium (KCl) may be used.)

Bichloride of Platinum ($PtCl_2$) produces a bright yellow crystalline precipitate of double chloride of platinum and potassium ($KCl, PtCl_2$). It is very sparingly soluble in water, and its formation is promoted by the presence of free hydrochloric acid. It is quite insoluble in strong alcohol. Previous to applying this test, the operator must assure himself of the absence of *ammonia*, and the solution should be concentrated.

Tartaric acid ($2HO, C_8H_4O_{10}$ or $2HO,\overline{T}$) added in excess produces a crystalline precipitate

$$KCl + 2HO,\overline{T} = KO,HO,\overline{T} + HCl$$

soluble in strong acids and in carbonated and caustic alkalies, but insoluble in tartaric and acetic acids: the formation of this salt is greatly facilitated by agitation.

Carbazotic or *trinitrophenic acid*, ($HO, C_{12}{H_2 \atop (NO_4)_3} O$) dissolved in alcohol produces a bright yellow crystalline precipitate ($KO, C_{12}H_2 (NO_4)_3 O$), which is freely soluble in boiling water, but very sparingly so in cold.

Perchloric acid (ClO_7) produces a sparingly soluble white crystalline precipitate (KO, ClO_7).

Before the blowpipe salts of potassa, if free from soda, heated on a platinum wire in the *inner* flame, tinge the *outer* flame *violet*. If soda salts be present, potassa may be detected by fusing a clear bead of borax with *oxide of nickel*, and then adding the mixture; the brown colour of the bead is changed to *blue*.

Characteristic.—The reaction with bichloride of platinum, and the violet coloration of the blowpipe flame.

28. Soda. (NaO.)

General characters of Hydrate of Soda (NaO,HO).—They are very similar to those of potassa. Its soluble salts afford no precipitates with any of the above reagents for potassa; but *Bimetantimoniate of potassa* ($2KO,SbO_5$) produces, in neutral and even in very dilute solutions, if well agitated, and provided no other oxide but potassa be present, a white crystalline precipitate.

(Solution of Sulphate of Soda or of Chloride of Sodium may be used.)

$$2(NaO,SO_3)+2KO,SbO_5=2(KO,SO_3)+2NaO,SbO_5.$$

Before the blowpipe soda salts are distinguished by the strong yellow colour which they communicate to the *outer* flame, which reaction is not prevented by a very considerable excess of potassa. According to Kobell, one part of chloride of sodium may hereby be detected in twenty-five or thirty parts of chloride of potassium.

29. Lithia. (LiO.)

General characters.—When pure this oxide is white. It is not so soluble in water as potassa or soda. Its solution rapidly absorbs carbonic acid when exposed to the air. Carbonate of lithia is very sparingly soluble in water; when a solution of a salt of lithia is mixed with one of phosphate of soda, the *double phosphate of soda and lithia* of very sparing solubility is precipitated. Phosphate of soda is therefore the characteristic test for this alkali.

Before the blowpipe salts of lithia are detected by the fine crimson tinge which they communicate to the *outer* flame, when heated in the *inner* flame on platinum wire. Potassa salts do not interfere with this reaction; but soda salts destroy it, substituting for the crimson their own peculiar yellow colour.

30. Ammonia (Oxide of Ammonium). (NH_4O.)

General characters.—The solution of pure ammonia in water is, when concentrated, highly caustic and alkaline. It has a powerful and penetrating smell, by which its presence can generally be detected. It attracts carbonic acid from the atmosphere. Most of its salts are soluble in water, and nearly all of them are totally volatilizable by heat. When present in an uncombined state, in quantity too small to be detected by the smell, its presence may be evinced by the production of white clouds when a feather dipped in strong acetic acid is held over the liquid. In salts of ammonia the compound

metal *ammonium* (NH_4) may be regarded as replacing the simple metals in other salts, thus :—

$$\underbrace{NH_3HCl}_{\text{Hydrochlorate of Ammonia.}} = \underbrace{(NH_4)Cl}_{\text{Chloride of Ammonium.}}$$

$$\underbrace{NH_3HO,SO_3}_{\text{Sulphate of Ammonia.}} = \underbrace{NH_4O,SO_3}_{\text{Sulphate of Ammonium.}}$$

Comportment of Ammoniacal Salts with reagents.

Bichloride of platinum produces a yellow crystalline precipitate ($NH_4Cl,PtCl_2$), having a great resemblance to the corresponding double salt of potassium.

Tartaric acid produces in concentrated solutions a crystalline precipitate ($NH_4O,HO,\overline{T}$) much more soluble than the corresponding potassa salt.

If to a solution of corrosive sublimate ($HgCl$) a sufficient quantity of iodide of potassium be added to redissolve the precipitate which is at first formed, and then considerable excess of caustic potassa, a solution is obtained which will detect one drop of chloride of ammonium in a pint of water, by the production of a yellowish turbidity. The reaction is considered to be expressed in the following equation :—

$$4(HgI,KO)+3(KO,HO,)+NH_3= (Hg_4NI,2HO)+7KI+4HO.$$

GROUP II.

The Alkaline Earths: Baryta, Strontia, Lime, and Magnesia.

31. BARYTA. ($BaO,HO.$)

General characters.—When pure, it is of a greyish-white colour ; it combines with water with the evolution of great heat, and is completely dissolved. Its concentrated aqueous solution deposits crystals. It is powerfully caustic and alkaline. It combines greedily with carbonic acid, forming a white insoluble compound, which is poisonous.

Comportment of soluble Barytic Salts with reagents.

(Solution of Chloride of Barium may be used.)

Alkaline carbonates produce a white precipitate (BaO,CO_2) soluble with effervescence in hydrochloric acid.

Ammonia and *caustic alkalies* do not produce any precipitate, provided atmospheric air be excluded.

Sulphuric acid and *soluble sulphates* produce, even in very dilute solutions, a white precipitate (BaO,SO_3), quite insoluble in water, and very sparingly so in hydrochloric acid.

Hydrofluosilicic acid (HF,SiF_2) produces after a time a colourless crystalline precipitate, almost entirely insoluble in free acids.

$$BaCl + HF,SiF_2 = BaF,SiF_2 + HCl.$$

Common phosphate of soda ($2NaO,HO,PO_5$) produces a white precipitate soluble in free acids.

Oxalic acid ($HO,C_2O_3 + aq$) and *soluble oxalates* produce, in tolerably concentrated solutions, a white precipitate ($BaO,C_2O_3 + aq$) soluble in free acids; the formation of this precipitate is favoured by ammonia.

Chromate of potassa ($KOCrO_3$) produces a yellow precipitate ($BaOCrO_3$), very sparingly soluble in nitric and hydrochloric acids.

Before the blowpipe, salts of barium, particularly the chloride, when heated on platinum wire at the point of the blue flame, communicate to the external flame a pale apple-green colour, which is not suppressed by the presence of salts of strontium, calcium, or magnesium, unless they greatly predominate.

Characteristic.—The reactions with sulphuric and hydrofluosilicic acids.

32. Strontia. (SrO.)

General characters.—It greatly resembles baryta; but it is not so heavy; neither is its hydrate so soluble in water; its aqueous solution is consequently less caustic.

Comportment of soluble Salts of Strontium with reagents.

(Solution of Chloride or Nitrate of Strontium may be used.)

Alkaline carbonates, the *caustic alkalies*, and *phosphate of soda* behave towards solutions of strontium salts precisely as towards solutions of salts of barium.

Sulphuric acid produces a white precipitate (SrO,SO_3) not altogether insoluble in water; in very dilute solutions, therefore, sulphate of lime and other soluble sulphates do not occasion an immediate precipitate.

Hydrofluosilicic acid occasions no precipitate even in concentrated solutions.

Chromate of potassa in cold and dilute solutions produces no precipitate; but, by boiling, a copious yellow precipitate (SrO,CrO_3) is determined.

Oxalic acid produces a white precipitate (SrO,C_2O_3+aq) even in dilute neutral solutions; in very dilute solutions the precipitate is immediately determined by the addition of ammonia.

Before the blowpipe, sulphate of strontia fuses to an opalescent mass, and colours the outer flame carmine-red. Chloride of strontium, heated on the ring of platinum wire at the apex of the blue flame, tinges the whole flame immediately deep-crimson; but as the assay fuses the colour disappears, by which it is distinguished from chloride of lithium. The presence of chloride of barium prevents the production of the coloured flame. Soluble salts of strontium, digested with alcohol, and inflamed, give rise to an intense and characteristic carmine-red colour.

Characteristic.—The red coloration of alcohol flame; the non-precipitation by hydrofluosilicic acid; and the gradual precipitation by sulphate of lime.

33. Lime. (CaO.)

When pure, it is white and infusible. It has an acrid, caustic, alkaline taste. It has a powerful affinity for water, in combining with which it emits great heat, and falls into a bulky powder. The hydrate of lime is far less soluble in water than the hydrates of the two preceding oxides, one part requiring for a perfect solution from 450 to 500 parts of water. The solution is slightly caustic, and gradually absorbs carbonic acid from the atmosphere, until the whole of the lime is converted into carbonate.

Comportment of solutions of Salts of Calcium with reagents.

(Solution of Chloride of Calcium may be used.)

The caustic and carbonated alkalies, and *phosphate of soda*, behave with calcareous solutions precisely as with solutions ot barium and strontium.

Sulphuric acid and the *soluble sulphates* occasion no precipitate in very dilute solutions; but, on the addition of alcohol, a precipitate (CaO,SO_3) immediately takes place: in concentrated solutions a bulky precipitate is produced, soluble, though not remarkably so, in nitric and hydrochloric acids.

Hydrofluosilicic acid does not produce any precipitate in solutions of calcareous salts.

Oxalic acid and the *soluble oxalates* occasion an immediate precipitate (CaO, C_2O_3) in neutral solutions, soluble in the mineral acids, but insoluble in acetic acid.

$$CaCl + NH_4O, C_2O_3 = CaO, C_2O_3 + NH_4Cl.$$

The formation of this precipitate is increased and quickened by the addition of ammonia.

Before the blowpipe, chloride of calcium, unless it has been fused, heated on the ring of the platinum wire, tinges the outer flame red, but the colour is more feeble than with chloride of strontium. Pure lime and the carbonate emit a very strong light. Soluble lime salts impart a yellowish-red tinge to the flame of alcohol.

Characteristic.—The reactions with oxalic and sulphuric acids.

34. MAGNESIA. (MgO.)

General characters.—It is a white infusible powder, possessed of a feeble but distinct alkaline reaction. Like lime, it is more soluble in cold than in hot water: 36,000 parts of boiling water, and 5142 parts at 32°, being required to dissolve one part of the earth. Caustic magnesia does not emit any heat on being moistened with water.

Behaviour of soluble Magnesium Salts with reagents.

(Solution of Sulphate of Magnesia may be used.)

Ammonia, in neutral solutions, occasions a white bulky precipitate (MgO, HO). If the solution be acid, or if ammoniacal salts be present, no precipitate takes place, in consequence of the property possessed by magnesia of forming double salts with ammonia.

Caustic potassa produces a voluminous flocculent precipitate, which disappears on the addition of chloride of ammonium; but, on boiling with excess of potassa, the precipitate reappears, in consequence of the decomposition of the ammoniacal salt.

Carbonate of soda produces in neutral solutions, and in the absence of ammoniacal salts, a white voluminous precipitate $2\,(HO, MgO) + 3\,(MgO, CO_2)$, which is increased by boiling, in consequence of the expulsion of the carbonic acid, which, in the cold, keeps a portion of magnesia in solution.

$$5(MgO, SO_3) + 5(NaO, CO_2) + 2HO =$$
$$2(MgO, HO) + (3MgO, CO_2) + 2CO_2.$$

Carbonate of ammonia, by boiling, and in the absence of ammoniacal salts, occasions a slight precipitate.

Sulphuric acid produces no precipitate (MgO,SO_3), being very soluble in water.

Phosphate of soda alone does not produce any precipitate in very dilute solutions; but, if *ammonia* be added, a crystalline precipitate of basic phosphate of magnesia and ammonia ($2MgO,NH_4O,PO_5$) is formed in highly diluted solutions.

$$2(MgO,SO_3)+2NaO,HO,PO_5+NH_3= \\ 2MgO,NH_4O,PO_5+2(NaO,SO_3).$$

This precipitate is insoluble in ammoniacal salts, but soluble in free acids.

Oxalate of ammonia, in the absence of ammoniacal salts, forms a white precipitate ($MgO,\bar{O}+2aq$).

Before the blowpipe, in the absence of other metallic oxides, salts of magnesium, when ignited on charcoal, then moistened with solution of protonitrate of cobalt, and again strongly *ignited*, acquire a feeble red tint.

Characteristic.—The reactions with phosphate of soda and nitrate of cobalt.

General Remarks on the Oxides of the Second Group.

From the property of magnesia to form soluble double salts with ammonia, this oxide may be kept in solution by the addition of chloride of ammonium and ammonia, while baryta, strontia, and lime are precipitated by carbonate of ammonia. The magnesia is detected in the filtered liquid by phosphate of soda. The immediate formation of a precipitate, on the addition of sulphate of lime, and the gradual formation of a crystalline precipitate on the addition of hydrofluosilicic acid, are characteristic of baryta. Strontia, in combination with baryta, is detected by converting both earths into chlorides, and digesting with absolute alcohol, in which chloride of barium is almost insoluble. Chloride of strontium is detected in the alcoholic solution by the carmine-red flame it communicates to the alcohol when ignited; and lime is detected by oxalate of ammonia. To discover the alkalies in the presence of the oxides of the second group, the baryta, strontia, and lime are first removed by boiling with carbonate of ammonia and caustic ammonia, and from the filtered liquid the magnesia is precipitated by baryta-water; the excess of baryta is removed by adding sulphuric acid in slight excess, and boiling; the whole is then filtered, and the clear filtrate evaporated to dryness in a platinum dish, and ignited; the residue is redissolved in

water, and the solution tested for potassa, soda, and lithia, by dividing it into three portions, and proceeding with each in the manner above directed for the discovery of the alkalies. A portion of the original solution is tested for ammonia, by heating with caustic potassa, and applying a feather moistened with strong acetic acid to the mouth of the tube.

GROUP III.

Metallic Oxides not precipitated by Hydrosulphuric Acid, but precipitated as Oxides by Sulphide of Ammonium.

(*Oxides of Aluminum, Yttrium, Glucinum, Thorinum, Zirconium, Chromium, Cerium, Titanium, and Tantalum.*)

35. OXIDE OF ALUMINUM (ALUMINA). (Al_2O_3.)

General characters.—When pure it is white, and in the state of powder it is light, and not at all compact. It has neither taste nor smell, but it adheres to the tongue, thereby occasioning a slight sense of astringency. By the heat produced by a stream of oxygen gas directed against the flame of a spirit-lamp, it slowly melts, and gives a limpid and colourless globule, which on cooling becomes crystalline. It is quite insoluble in water, although it possesses a powerful affinity for that fluid, from which it can only be deprived by heating to redness. It condenses moisture from the atmosphere in a remarkable manner. The hydrate of alumina has a strong affinity for vegetable colouring principles.

Comportment of soluble Aluminum Salts with reagents.

(Solution of Sulphate of Alumina may be used.)

Sulphide of ammonium produces a white voluminous precipitate of hydrate of alumina, soluble in potash, hydrosulphuric acid being evolved.

$$Al_2O_3,3SO_3+3(NH_4S)+6HO=$$
$$Al_2O_3,3HO+3(NH_4O,SO_3)+3HS.$$

Potassa and *soda* produce in neutral solutions a bulky precipitate of hydrate of alumina (Al_2O_33HO), entirely soluble in excess of the precipitant, but again precipitated by chloride of ammonium which destroys the solvent.

$$KO+NH_4Cl=KCl+NH_4O.$$

Ammonia occasions the same precipitate very sparingly soluble in excess of the precipitant.

The alkaline carbonates precipitate hydrate of alumina with the evolution of carbonic acid.

Phosphate of soda produces a precipitate soluble in free acids and in potassa.

Silicate of potassa (soluble glass) produces a precipitate (silicate of alumina) in solutions of this oxide in potassa.

Before the blowpipe, alumina and many of its compounds may be detected by heating the assay on charcoal, then moistening it with solution of protonitrate of cobalt, and again heating it strongly in the oxidizing flame. A fine *blue* colour is produced.

Characteristic.—The reactions with sulphide of ammonium, potassa, and nitrate of cobalt.

36. Oxide of Glucinum. (Gl_2O_3.)

General characters.—This earth, when pure, has neither taste nor smell; it is insoluble in water, and infusible; but it does not harden in the fire like alumina, neither is the paste which it forms with water *plastic*. Its soluble salts have a sweet taste with a slight astringency. They do not yield an alum with sulphate of potassa.

Comportment of Salts of Glucinum with reagents.

Potassa and *soda* precipitate hydrate of glucina soluble in excess of the precipitants, but again precipitated by long boiling. Chloride of ammonium also precipitates the earth from its alkaline solution.

Ammonia produces a voluminous precipitate, insoluble in excess of precipitant; the presence of chloride of ammonium does not prevent the formation of this precipitate.

The carbonated alkalies occasion a bulky precipitate, which is soluble in great excess of the precipitants, but more easily in carbonate of ammonia than in carbonate of potassa.

Phosphate of soda produces a voluminous precipitate.

Before the blowpipe, glucina and its salts cannot well be detected; they do not become blue when strongly heated with protonitrate of cobalt, like alumina.

Sulphide of ammonium precipitates hydrate of glucina with the extrication of sulphuretted hydrogen.

Glucina is distinguished from *alumina* by its reaction with

alkaline carbonates; by its salts not yielding *alum* with sulphate of potash; and by its not becoming blue when heated before the blowpipe with nitrate of cobalt.

37. Oxide of Yttrium. (YO.)

General characters.—This rare earth is of a pale-yellow colour. Its specific gravity is 4·842; it is therefore heavier than baryta, the specific gravity of which is 4·000. It is soluble in acids after ignition. It gradually absorbs carbonic acid from the atmosphere. Many of its salts, and especially the sulphate, have a faint amethyst-red colour, and a sweetish taste. According to Mosander, three bases have been included under the name of *yttria*, one of which he calls *erbia*, and the other *terbia*.

Comportment of Salts of Yttrium with their reagents.

Potassa, soda, and *ammonia* produce white voluminous precipitates, insoluble in excess of the precipitants, even by heat.

The carbonated alkalies produce precipitates soluble in excess of the precipitants, particularly in carbonate of ammonia; from the latter solution crystals of double carbonate of ammonia and yttria may be obtained.

Sulphate of potassa produces, after a time, a precipitate, which is completely redissolved on the addition of water, even in the presence of sulphate of potassa.

Phosphate of soda produces a precipitate soluble in hydrochloric acid, from which it is again thrown down by boiling.

Ferrocyanide of potassium (K_2FeCy_3) occasions a white precipitate.

Before the blowpipe, yttria cannot with certainty be detected. According to Plattner, phosphate of yttria may be recognized by giving a regulus of *phosphide of iron* with boracic acid and iron, and from the difficulty with which it is dissolved by microcosmic salt.

38. Oxide of Thorinum. (ThO.)

General characters.—This rare earth is, when quite free from manganese, *white.* It is the heaviest of all the earths, its specific gravity being 9·402. Its solutions have an astringent taste; it absorbs carbonic acid from the air. When moist, the hydrate dissolves readily in acids; but after having been dried, it is acted on with difficulty. The calcined earth is only attacked by hot sulphuric acid. Sulphate of thorina is, accord-

ing to Berzelius, distinguished from all other oxidized bodies known, by its property of being precipitated by boiling, and slowly redissolving on cooling.

Behaviour of solutions of Oxide of Thorinum with reagents.

Potassa and ammonia produce a quickly subsiding precipitate, insoluble in excess of the precipitants.

The carbonated alkalies produce a precipitate dissolving readily in excess of the precipitants.

Sulphate of potassa produces a double salt, insoluble in water containing sulphate of potassa.

Ferrocyanide of potassium occasions a heavy white precipiate, soluble in acids.

Before the blowpipe, the reactions of thorina have not been studied.

39. Oxide of Zirconium. (Z_2O_3.)

General characters.—When pure and calcined, glucina is a white infusible powder; when ignited, it becomes brilliantly incandescent: it is sufficiently hard to scratch glass. Its specific gravity is 4·3. After having been ignited, it is soluble only in concentrated sulphuric acid. Its soluble salts have a purely astringent taste, without any sweetness.

Comportment of Salts of Oxide of Zirconium with reagents.

Potassa and ammonia produce precipitates insoluble in excess of the precipitants.

The carbonated alkalies produce precipitates slightly soluble in excess of the precipitants; the hydrate of zirconia is soluble in carbonate of ammonia, but very sparingly so in the carbonates of the fixed alkalies.

Ferrocyanide of potassium occasions a white precipitate.

Sulphate of potash produces a white double salt, almost insoluble in water.

Before the blowpipe, the reactions of *zirconia* are similar to those of *glucina,* from which it is distinguished by the vivid white light which it emits when ignited.

40. Sesquioxide of Chromium. (Cr_2O_3.)

General characters.—After ignition it is of a fine green colour, and is only soluble in hot sulphuric acid: the hydrate is of a greyish-green colour, and is readily soluble in acids, forming green solutions under reflected, and red by transmitted,

light; but if the hydrate has been strongly dried, but not ignited, it dissolves in acids with difficulty.

Comportment of solutions of Salts of Chromium with reagents.

(Solution of Sesquichloride of Chromium, Cr_2Cl_3, may be used.)

Sulphide of ammonium produces a bluish-green precipitate of hydrate of sesquioxide of chromium, sulphuretted hydrogen being disengaged.

$$Cr_2Cl_3 + 3NH_4S + 6HO = Cr_2O_3,3HO + 3NH_4Cl + 3HS.$$

Potassa produces a bluish-green precipitate ($Cr_2O_3,3HO$), readily soluble in an excess of the precipitant, forming a green solution, from which the green anhydrous oxide is re-precipitated by boiling, either alone or with chloride of ammonium.

Ammonia and *carbonate of ammonia* produce a bluish-green precipitate, partially soluble in the precipitant, to which it imparts a red colour; but the precipitation is complete by boiling the ammoniacal solution.

Carbonate of potassa or soda produce a bluish-green precipitate, soluble completely in considerable excess of the precipitant, and not re-precipitated by boiling.

Phosphate of soda produces a light green precipitate.

Any compound of oxide of chromium when fused with nitre gives rise to the formation of chromate of potassa (KO,CrO_3), which is soluble in water, and to which it communicates a yellow colour.

Before the blowpipe, the presence of oxide of chromium is easily detected by the beautiful green bead obtained when it is heated with borax or microcosmic salt, both in the inner and outer flame: oxide of copper gives also a green bead, but only in the outer flame.

Characteristic.—The colour of its salts; their conversion into chromic acid; and the reaction in the blowpipe flame.

41. Titanic Acid. (TiO_2.)

General characters.—It is a white, insipid, infusible powder; when heated, it assumes a fine yellow colour, but again becomes colourless on cooling. It reddens infusion of turnsole even after having been exposed to a red-heat, though the calcination renders it insoluble in acids.

Comportment of solutions of Titanic Acid with reagents.

Ammonia precipitates a white gelatinous hydrate, soluble with great readiness in acids, and soluble also in small quantities

in the carbonated alkalies: it is precipitated from its solution in carbonate of ammonia by long boiling: its solution in carbonate of potassa or soda is precipitated by boiling with sal-ammoniac. Titanic acid is precipitated as a heavy white powder from its acid solutions by continued boiling: this precipitate cannot, however, be washed on a filter with pure water (Rose): according to Berzelius, it can be completely precipitated from its solution in sulphuric acid by long-continued boiling.

The caustic alkalies and *sulphide of ammonium* do not precipitate titanic acid in the presence of a sufficient quantity of tartaric acid.

Ferrocyanide of potassium produces a red-brown precipitate.

Sulphite of ammonia (NH_4O,SO_2), aided by a gentle heat, completely precipitates titanic acid. If, in a solution of titanic acid, or an alkaline titanate, in hydrochloric acid, a bar of *zinc*, *tin*, or *iron* be placed, the titanic acid will be reduced to *sesquioxide of titanium* (Ti_2O_3), and the liquor will acquire a blue or violet colour; after a time, however, a violet powder is precipitated, and the liquid becomes colourless. This is characteristic of titanic acid.

Before the blowpipe, pure titanic gives in the reduction flame, with microcosmic salt, a violet bead; the reaction is observed better on adding metallic tin; in the presence of peroxide of iron the glass appears, when strongly heated in the reducing flame, yellow, and on cooling, red; with borax no alteration is produced by the presence of iron.

General Remarks on the Oxides of the Third Group.

Alumina and *glucina* are both dissolved readily by caustic potassa; but the two earths are distinguished from each other by the latter being precipitated from its alkaline solution by boiling, and by its hydrate being soluble in carbonate of ammonia. *Yttria*, *thorina*, and *zirconia* are not soluble in caustic potassa; *yttria* is distinguished from the other two earths by the double salt which it forms with sulphate of potassa being soluble in solution of sulphate of potassa; whereas the double salts formed by thorina and zirconia are not soluble in sulphate of potassa. These two latter earths are not very easily distinguished from each other; but the precipitate produced by carbonated alkalies in solutions of *thorina* is much more soluble in carbonate of potassa than the corresponding precipitate in solution of *zirconia*. *Thorina* is, moreover, more than double the density of *zirconia*, which is distinguished again by the glaring

white light which it produces when strongly ignited. The colour of the salts of *chromium*, and their behaviour before the blowpipe, is quite sufficient to distinguish this oxide from all the other members of the group. *Titanic* acid is distinguished by the blue colour produced on bringing a rod of zinc or iron into contact with its acid solutions.

This group may be subdivided into two sections by the comportment of its members with caustic potassa; thus *alumina*, *glaucina*, and *oxide of chromium*, are soluble in this alkali: the other members are insoluble.

GROUP IV.

Metallic Oxides not precipitated from their acid solutions by Hydrosulphuric Acid, but completely precipitated by Sulphide of Ammonium as Sulphides.

(*Oxides of Zinc, Nickel, Cobalt, Manganese, Iron, and Uranium.*)

42. Oxide of Zinc. (ZnO.)

General characters.—When pure it is white; it becomes yellow when heated, but on cooling its whiteness usually returns, though sometimes it retains it yellow tinge. It is sometimes obtained crystalline, and is then always yellow. When the metal is burned in the air, the oxide is obtained of snowy whiteness, and in light flocks. In this state it has been called "philosophical wool." It has a remarkable affinity for alumina; a combination of the two oxides in atomic proportions is met with in the mineral kingdom crystallized in regular octahedra, and is known under the name of *Gahnite*.

Comportment of solutions of Salts of Zinc with reagents.

(Solution of Sulphate of Zinc may be used.)

Potassa and ammonia produce in neutral solutions a white gelatinous precipitate (ZnO,HO), readily soluble in an excess of the precipitants.

Hydrosulphuric acid produces in neutral solutions a white precipitate (ZnS); in acid solutions no precipitate is formed.

Sulphide of ammonium completely precipitates salts of zinc, as ZnS, insoluble in an excess of the precipitant, as well as in *potassa* and *ammonia*.

The carbonates of the fixed alkalies precipitate basic carbonate

of zinc ($3HO,ZnO + 2ZnO,CO_2$), quite insoluble in an excess of the precipitants, but soluble in *potassa* and in *ammonia*. The presence of any salt of the latter prevents the formation of this basic salt, a soluble double salt of zinc and ammonia being formed.

Carbonate of ammonia produces a white precipitate, soluble in an excess of the precipitant.

Phosphate of soda produces a precipitate soluble in acids, and in *potassa* and in *ammonia*.

Oxalic acid and *binoxalate of potassa* occasion precipitates which are soluble in acids and in fixed alkalies, but the formation of which is not prevented by sal-ammoniac.

Ferrocyanide of potassium produces a white gelatinous precipitate, insoluble in free hydrochloric acid.

Ferridcyanide of potassium produces a yellowish-red precipitate, soluble in hydrochloric acid.

Before the blowpipe, zinc salts are easily detected. Heated with carbonate of soda on charcoal in the reducing flame metallic zinc is produced, which volatilizes, and on coming into contact with the air is again oxidized, and the charcoal becomes covered with a sublimate, which, when hot, is yellow, but on cooling white, and gives when heated in the oxidating flame with a few drops of protonitrate of cobalt a beautiful and characteristic green colour.

Characteristic.—The reactions with *potash* and *sulphuretted* hydrogen, and before the blowpipe.

43. Oxide of Nickel. (NiO.)

General characters.—The pure oxide is of a deep ash-grey colour; it is not magnetic; it dissolves readily in acids; its hydrate is of an apple-green colour.

Comportment of solutions of Salts of Nickel with reagents.

(Solution of Sulphate of Nickel may be used.)

Potash produces a bright green precipitate, insoluble in an excess of the precipitant, but soluble in carbonate of ammonia.

Ammonia precipitates the same green hydrate, but an excess redissolves it, forming a clear blue solution, from which *potassa* again precipitates the hydrate.

Hydrosulphuric acid does not precipitate acid solutions of nickel. In neutral solutions, after a time, an inconsiderable black precipitate is formed; but in the presence of an alkaline

acetate, aided by a gentle heat, sulphuretted hydrogen effects a complete precipitation.

Sulphide of ammonium produces a black precipitate (NiS), partially soluble in an excess of the precipitant; hence, after the subsidence of the precipitate, the fluid remains black.

Alkaline carbonates produce a pale green precipitate, soluble in carbonate of ammonia.

Phosphate of soda occasions a very pale yellow precipitate.

Ferrocyanide of potassium produces a pale yellowish-green precipitate.

Cyanide of potassium throws down a greenish-white precipitate ($NiCy$), which an excess redissolves into a brownish-yellow liquid ($NiCy, KCy + HCl = NiCy + KCl + HCy$); on the addition of a mineral acid, cyanide of nickel is again precipitated, and hydrocyanic acid set free.

Before the blowpipe, salts of nickel, heated in the outer flame with borax or microcosmic salt, give a reddish-coloured bead. The addition of nitre changes the colour to dark purple or blue: heated in the inner flame on charcoal with carbonate of soda, reduction takes place, and renders the bead grey.

Characteristic.—The reactions with *ammonia* and *cyanide of potassium*.

44. Oxide of Cobalt. (CoO.)

General characters.—As obtained by the calcination of the carbonate, it is of an ash-grey colour; as obtained by the combustion of the metal, it is blue or greyish-blue; as precipitated from its solutions by caustic *potassa*, it has a fine blue colour. When this precipitate is boiled for some time, it assumes by degrees a violet, and finally a dirty red tinge, which, according to Proust, is the hydrate: the blue precipitate is considered by some chemists to be a basic salt. It dissolves by fusion with vitreous fluxes, communicating to them a magnificent blue colour, or if in excess, black.

Comportment of solutions of Salts of Cobalt with reagents.

Potassa produces a blue precipitate, insoluble in an excess of the precipitant, but soluble in carbonate of ammonia; the precipitate becomes green by exposure to the air, and dingy-red when boiled.

Ammonia produces a blue precipitate, which an excess redissolves, forming a solution which is at first green, but which by

exposure to the air becomes brown; if sal-ammoniac be present in sufficient quantity, neither *potassa* nor *ammonia* produce any precipitate, though, if air have access, the solution gradually becomes brown.

The alkaline carbonates produce a red precipitate, which upon being boiled becomes blue.

Phosphate of soda occasions a blue precipitate.

Ferrocyanide of potassium gives a green precipitate, which gradually turns grey.

Ferridcyanide of potassium gives a dark reddish-brown precipitate.

Hydrosulphuric acid in acid solutions occasions no precipitate: in neutral solutions, after a time, a slight black precipitate, the solution acquiring a dark colour.

Cyanide of potassium throws down CoCy as a brownish white precipitate, easily soluble in excess of the precipitant; on the addition of hydrochloric acid no precipitate takes place, the whole of the cobalt passing into the state of *cobalto-cyanide of potassium;* thus:—

$$2CoCy + 3KCy + HCy = (Co_2Cy_6K_3) + H,$$

which is not decomposable by weak acids.

Sulphide of ammonium produces a black precipitate, insoluble in excess.

Before the blowpipe, salts of cobalt are distinguished by the beautiful blue colour they communicate to borax and microcosmic salt, in both oxidating and reducing flames. Heated with carbonate of soda in the reducing flame, a grey powder (metallic cobalt) is produced.

Characteristic.—The reactions with potash, ammonia, and cyanide of potassium, and before the blowpipe.

45. Oxide of Manganese. (MnO.)

General characters.—It is of a greyish-green colour. When prepared by igniting the carbonate or oxalate in an atmosphere of hydrogen, it absorbs oxygen from the air, gradually becoming brown. The oxide, prepared by fusing the chloride with anhydrous carbonate of soda, undergoes no alteration by exposure to the air. The hydrate when first precipitated is white, but on exposure to the air it gradually becomes brown. This oxide possesses, in common with magnesia and oxide of iron, the property of only being partially precipitated by ammonia, and of carrying with it a portion of silicic acid when precipi-

tated from a liquid holding this acid in solution. The salts of oxide of manganese are sometimes colourless, and sometimes of a pale rose-colour.

Comportment of solutions of Salts of Manganese with reagents.

(Solution of Sulphate of Manganese may be used.)

Potash and ammonia produce precipitates which at first are white, but soon become coloured, first yellow, then brown, and finally nearly black: if ammoniacal salts be present, *ammonia* occasions no precipitate, and *potassa* only a partial one, which slowly becomes brown by exposure to the air. A clear ammoniacal solution containing oxide of manganese gradually gets turbid by exposure to the air, brown hydrated sesquioxide of manganese being deposited.

The carbonated alkalies produce a white precipitate of carbonate of manganese, which is permanent in the air, and sparingly soluble in sal-ammoniac.

Phosphate of soda produces a white precipitate persistent in the air.

Ferrocyanide of potassium produces a pale red precipitate, soluble in free acids.

Ferridcyanide of potassium gives a brown precipitate, insoluble in free acids.

Hydrosulphuric acid does not precipitate either acid or neutral solutions.

Sulphide of ammonium produces a flesh-red precipitate ($Mn\,S$), insoluble in excess, but soluble in mineral acids and even in strong acetic acid; by exposure to the air it becomes oxidized, finally assuming a brownish-black colour.

Puce-coloured oxide of lead (binoxide), heated with pure dilute nitric acid, produces when added to a solution of a salt of manganese, a fine crimson colour (permanganic acid, $Mn_2\,O_7\,HO$).

By fusing any salt of manganese on platinum foil with a mixture of nitre and carbonate of soda, *manganate of soda* of a fine green colour is produced; the smallest portion of manganese may in this manner be detected.

Before the blowpipe, fused in the oxidating flame with borax or microcosmic salt, salts of manganese give an amethyst-coloured bead, the colour of which disappears in the reducing flame, but may again be produced in the oxidating flame.

Characteristic.—The reactions with *sulphide of ammonium* and *binoxide of lead*, and with carbonate of soda with heat.

46. Protoxide of Iron. (FeO.)

General characters.—This oxide, which is only obtained pure with extreme difficulty, is black, and has frequently a metallic lustre; it is brittle; fuses at a high temperature; and on cooling is converted into a brittle, brilliant, but not vitreous mass. It is dissolved in acids with great difficulty, after having been exposed to a red-heat; but the salts formed are identical with those obtained by dissolving the metal itself in the respective acids. It is very feebly magnetic, by which it is distinguished from the *ferrosoferric oxide* (FeO,Fe_2O_3), which is strongly magnetic. It combines with water, forming a hydrate which, when pure, is white; but by contact with the atmosphere it speedily becomes coloured; first grey, then green, then bluish-black, and finally yellow. When boiled in an hermetically closed vessel, it parts with its water, and becomes black. It is the basis of all the protosalts of iron.

Comportment of Salts of Protoxide of Iron with reagents.

(Solution of Protosulphate of Iron may be used.)

Potassa and *ammonia* produce a flocculent precipitate of hydrated protoxide of iron, which at first is nearly white, but which readily becomes coloured by exposure to the air. The presence of ammoniacal salts prevents the precipitation of oxide of iron by *ammonia*, and in some degree by *potassa*.

Alkaline carbonates produce a white carbonate, gradually becoming coloured, though not so readily as the oxide. It is soluble in sal-ammoniac, but a coloured precipitate makes its appearance by exposure to the air.

Phosphate of soda produces a white precipitate, which after a time becomes green.

Ferrocyanide of potassium produces a precipitate, which, if air be entirely excluded, is white (K,Fe_3Cfy_2); but, if air or a small quantity of sesquioxide of iron be present, it has a blue tinge; by exposure to the air, or by contact with nitric acid or chlorine, it absorbs oxygen, and gives rise to the formation of Prussian blue. The transformation will be understood from the following equations:—

$$(a.)\ 3FeCl + 2K_2,Cfy = 3KCl + KFe_3Cfy_2.$$

$$(b.)\ 3(K,Fe_3Cfy_2) + 4O = 2(Fe_4Cfy_3) + 3KO + FeO.$$

Prussian blue is insoluble in hydrochloric acid; its colour is discharged by the fixed caustic alkalies.

Ferridcyanide of potassium (K_3Cfy_2) produces a beautiful blue precipitate, insoluble in acids, but easily decomposable by alkalies. The composition of this substance is Cfy_2F_3, and it is thus formed:—

$$3FeCl + K_3Cfy_2 = 3KCl + Cfy_2Fe_3 \text{ (Turnbull's blue).}$$

Hydrosulphuric acid does not precipitate acid solutions of oxide of iron; and neutral compounds very incompletely.

Sulphide of ammonium produces a black precipitate, speedily becoming brown by exposure to the air. It is insoluble in alkalies and alkaline sulphides, but easily soluble in mineral acids.

Before the blowpipe, protosalts of iron heated on charcoal with borax or microcosmic salt in the oxidating flame give dark-red beads, becoming lighter on cooling; in the inner flame the colour produced is green, which disappears on cooling, if the metal be not present in too large quantity. When fused with soda on charcoal in the reducing flame, a metallic magnetic powder is obtained.

Characteristic.—The reactions with *ferrocyanide and ferridcyanide of potassium.*

47. Sesquioxide of Iron. (Fe_2O_3.)

General characters.—Its colour and physical appearance differ according to its mode of preparation. It is met with in nature of a grey colour, and crystalline; as prepared by the calcination of the subsulphate of the sesquioxide, it has a fine red colour; from the sulphate its colour is deeper, and when made from the nitrate it is brownish-black; and it is sometimes met with quite black. By the action of a high heat it is converted into ferrosoferric oxide (FeO, Fe_2O_3) with the disengagement of oxygen gas. It does not dissolve very readily save in concentrated acids, after having been strongly heated, though much more easily than the protoxide. It is not easily precipitated from its solutions by means of an alkali or an earth. If too little alkali be added, a subsalt is thrown down; if too much, a portion is precipitated with the oxide. When iron is oxidized by degrees in contact with a large quantity of water, a hydrate of the sesquioxide of a clear orange colour is formed.

Comportment of solutions of Salts of Sesquioxide of Iron with reagents.

(Solution of Sesquichloride of Iron may be used.)

Potassa and ammonia produce a voluminous reddish-brown hydrate, insoluble in excess. The precipitation is prevented by the presence of organic acids, sugar, etc.

$$Fe_2Cl_3 + 3NH_3 + 6HO = Fe_2O_3,3HO + 3NH_4Cl.$$

The *carbonated alkalies* throw down precipitates of rather a lighter colour, carbonic acid being at the same time disengaged.

Phosphate of soda produces a white precipitate of phosphate of sesquioxide of iron of varying composition, which becomes brown, and finally dissolves on the addition of ammonia.

Ferrocyanide of potassium produces a beautiful blue precipitate (Fe_4Cfy_3) by the following reaction :—

$$2FeCl + 3K_2Cfy = Fe_4Cfy_3 + 6KCl.$$

Sulphocyanide of potassium produces a rich blood-red colour, even in very dilute solutions ($FeCyS_2$).

Hydrosulphuric acid produces in neutral solutions a white deposit of sulphur, the sesquioxide being reduced to protoxide thus :—

$$Fe_2O_3 + HS = 2FeO + HO + S.$$

Sulphide of ammonium produces in neutral solutions a black precipitate, insoluble in excess, and becoming brown by exposure to the air. This precipitation is preceded by the reduction of the sesquioxide into protoxide.

Before the blowpipe, salts of sesquioxide of iron behave in the same manner as those of the protoxide.

Characteristic reactions.—Those with *ferrocyanide and sulphocyanide of potassium.*

48. Sesquioxide of Uranium. (Ur_2O_3.).

General characters.—The hydrate is a beautiful yellow powder, soluble in acids, forming fine yellow solutions; heated to about 300°, it loses its water and becomes anhydrous; it then has a bright brick-red colour. Heated above that temperature, it loses oxygen and becomes converted into *uranoso-uranic oxide* (UrO, Ur_2O_3) of a deep-grey colour. Sesquioxide of uranium reddens moistened turnsole paper, though it blues paper stained red with infusion of logwood. It produces, therefore, the reaction of acid and base. According to Berzelius, this substance should more properly be called *uranic*

acid; its properties being rather those of an electro-negative than of an electro-positive oxide. It forms definite compounds with bases, all of which are insoluble in water; and, when precipitated from its solution in an acid by means of an alkali, the latter is divided into two portions, and the precipitate obtained is a *uranate.*

Comportment of solutions of Salts of Sesquioxide of Uranium with Reagents.

(Solution of the Nitrate of the Sesquioxide of Uranium may be used.)

Caustic alkalies precipitate *uranates* of the bases of a pale yellow colour.

Alkaline carbonates produce pale yellow precipitates, soluble in excess of carbonate of ammonia, but again precipitated by boiling.

Sulphite of ammonia produces at a boiling temperature a yellow precipitate.

Ferrocyanide of potassium gives a red brown precipitate.

Hydrosulphuric acid reduces salts of sesquioxide with the deposition of sulphur; but sesquioxide is again produced by exposure to the atmosphere, or by the action of oxidizing agents.

Sulphite of ammonia produces a black precipitate.

Before the blowpipe, heated alone on charcoal, sesquioxide of uranium is converted into protoxide; heated with microcosmic salt on platinum wire in the oxidating flame, it dissolves, producing a clear yellow glass, which on cooling becomes green.

Characteristic.—The reactions with the *caustic* and *carbonated alkalies* and with *ferrocyanide of potassium.*

General Remarks on the Oxides of the Fourth Group.

Of the seven oxides constituting this group, *oxide of zinc* alone is soluble in *caustic potassa.* It is thus readily separated from the other six, and it is distinguished from *alumina, oxide of chromium,* etc., members of the third group, by its being again precipitated from its alkaline solution by sulphuretted hydrogen. *Oxides of zinc, cobalt, iron,* and *manganese* form with *ammonia* soluble double salts not precipitable by alkalies. *Oxide of iron* is easily eliminated from the other three oxides, by converting it into *sesquioxide,* by boiling with nitric acid or with *chlorate of potash.* It is then completely precipitated by *ammonia,* provided no non-volatile organic matter be present. The same is the case with *sesquioxide of uranium. Hydrate of*

oxide of nickel is dissolved by *ammonia*, but again precipitated by *potassa*. *Hydrated oxide of nickel* and *hydrated oxide of cobalt* are both soluble in *carbonate of ammonia*, which is not the case with *hydrated protoxide of manganese*, which may thus, therefore, be separated from them. The perfect separation of *oxide of nickel* from *oxide of cobalt* is attended with great difficulties. The presence of *nickel* may be recognized by the behaviour of the solution of its cyanide in cyanide of potassium with hydrochloric acid, which precipitates it, the same not being the case with cyanide of cobalt. In the former case a double cyanide of nickel and potassium (NiCy, KCy) is formed; but in the latter, with the presence of free hydrocyanic acid, a *cobaltocyanide of potassium* is formed. Thus:—

$$2\,CoCy + 3\,KCy + HCy = K_3CO_2Cy_6 + H.$$

Now, though the solution of cyanide of cobalt in cyanide of potassium is not precipitated by an acid, it may be so in the presence of nickel, and if that metal be present in the proportion of three equivalents to two equivalents of cobalt, the whole of the latter will be precipitated,—the three equivalents of nickel replacing the three equivalents of potassium in the cobaltocyanide of potassium, and giving rise to cobaltocyanide of nickel ($N_3Co_2Cy_6$). Thus:—

$$3(NiCy + KCy) + Co_2K_3Cy_6 = 6\,KCy + Co_2Ni_3Cy_6.$$

The blowpipe is, moreover, an infallible test of the presence of *oxide of cobalt*.

GROUP V.—Section A.

Metallic Oxides precipitated from their solutions, whether acid, alkaline, or neutral, as Sulphides by Hydrosulphuric Acid.

(*Oxides of Lead, Silver, Mercury, Bismuth, Cadmium, Copper, Palladium, Iridium and Osmium.*)

49. Protoxide of Lead. (PbO.)

General characters.—When pure, this oxide is yellow, but its powder has a reddish tint. When certain lead salts, as the subnitrate and oxalate, are decomposed by heat without fusion, they furnish an oxide of a pure sulphur-yellow colour, which by trituration becomes red: in this state it is sometimes called

massicot. By allowing a solution of oxide of lead, in caustic soda, to remain for some months exposed to the air, white, semitransparent, dodecahedron crystals of anhydrous oxide may be obtained. The same crystals, according to Payen, are formed on mixing a dilute solution of acetate of lead, with great excess of caustic ammonia, and exposing to the rays of the sun. Protoxide of lead becomes of a deep-red colour when heated, regaining its primitive colour on cooling: at a red heat it fuses and cools in semitransparent, deep brick-red, crystalline scales; at a still higher temperature it undergoes partial decomposition, the metal being reduced. It absorbs carbonic acid slowly from the air; hence an effervescence generally attends its solution in an acid. Pure water is capable of retaining in solution from $\frac{1}{7000}$ to $\frac{1}{12000}$ of oxide of lead. The hydrate is white, and absorbs carbonic acid rapidly from the air. It loses its water at about 300°. Protoxide of lead combines with alkalies and earths; its combinations with potassa and soda are crystallizable. It enters into fusion with, and dissolves, the earths with great facility. Its best solvent is nitric or acetic acid.

Comportment of solutions of Salts of Lead with reagents.

(Solution of Nitrate or Acetate of Lead may be used.)

Potassa and ammonia produce white precipitates, which are basic salts, soluble in a great excess of *potassa*, but insoluble in ammonia.

The *carbonated alkalies* produce white precipitates, soluble in *potassa.*

Phosphate of soda occasions a white precipitate, soluble in *potassa.*

Oxalic acid produces, in neutral solutions, a white precipitate.

Ferrocyanide of potassium produces a white precipitate, soluble in potassa.

Iodide of potassium produces a yellow precipitate, soluble in great excess by heat, and separating on cooling, in magnificent yellow spangles. ($PbI.$)

Chromate of potassa produces a fine yellow precipitate, soluble in potassa, but insoluble in dilute nitric acid. (PbO, CrO_3.)

Hydrochloric acid and *soluble chlorides* produce a heavy white precipitate, soluble in boiling water, out of which it separates, on cooling, in brilliant crystals. This precipitate is soluble in *potassa.* ($PbCl.$)

Hydrosulphuric acid produces a black precipitate, both in acid and neutral solutions. (PbS.)

Sulphide of ammonium produces a black precipitate, insoluble in excess.

Sulphuric acid and *soluble sulphates* produce a white precipitate (PbO,SO_3) sparingly soluble in dilute acids, but soluble in solution of potassa, and assuming a black colour when moistened with hydrosulphuret of ammonia.

Before the blowpipe, on charcoal, mixed with carbonate of soda, salts of lead are immediately reduced, furnishing a metallic globule, which gradually sublimes, leaving a yellow residue. The metallic globule can easily be flattened under the hammer.

Characteristic reactions.—Those with *sulphuric* and *hydrochloric acids* and with *sulphuretted hydrogen*.

50. *Poisoning by Lead. Detection of the Metal in Organic Mixtures.*

The vegetable acids and alkaline and fatty substances dissolve protoxide of lead, forming salts of a poisonous character; and as the glaze of earthenware vessels employed for culinary purposes usually contains oxide of lead, the accidental adulterations of food and liquids which have been prepared or allowed to remain for some time in such vessels, are not of uncommon occurrence. Pies which have been baked in a newly glazed vessel have been known to become contaminated with oxide of lead, and to have occasioned the peculiar symptoms of lead poisoning in the persons partaking of them. The presence of the deleterious metal in the food, in cases of this kind, is proved by moistening the articles with sulphide of ammonium, by which they become of a more or less brown colour; and lead is detected in the glaze of the vessels by boiling in them acetic acid or caustic potass, by which the oxide becomes dissolved. Cases of poisoning by the accidental impregnation of articles of drink with oxide of lead would probably be more frequent, but for the property possessed by some vegetable substances, particularly those containing tannin or gallic acid, of forming insoluble compounds; but, as a general rule, no substances used for food should be kept in leaden vessels, neither should liquids containing free acid, or in which a vegetable acid is likely to be formed, be kept for any length of time in a newly glazed earthenware vessel. Dr. Christison relates a case in

which lead colic, paralysis, and death were occasioned by eating the cream which formed on milk kept in a leaden cistern. Wines have been accidentally impregnated with oxide of lead, in consequence of the bottles having been cleaned with shot, and some of the pellets left behind; the impregnation is not very likely to occur to any injurious extent in good wine, such as port or sherry, but in acid wines, such as currant or gooseberry, a sufficient quantity of the oxide might be dissolved to produce serious consequences. Wines have been also designedly adulterated with oxide of lead, to remove their acidity, and to give them a sweet taste; this fraud was formerly practised to a considerable extent. It was detected and exposed in France by Fourcroy. In this country it does not appear to have been pursued to any material extent; though, before the poisonous nature of lead compounds was generally known, British wines must have been frequently adulterated, for, in an old cookery book, quoted by Sir G. Baker, the following recipe occurs:—

"*To hinder Wine from turning.*—Put a pound of melted lead in fair water into your cask, pretty warm, and stop it close."

Cider, also, is apt to become impregnated with salts of lead, in consequence of the metal being used for various purposes in the construction of the cider house; and although the source of the contamination was long ago pointed out by Sir George Baker, so recently as 1841 a set of cases which presented the incipient symptoms of lead colic were traced by MM. Chevalier and Ollivier to cider having been adulterated with lead to the amount of nearly two grains and a half per quart, in consequence of a publican having kept his cider for two days in a vessel lined with lead. The poisonous salt was found to be *malate*. *New rum* is often found to contain lead, which it derives from the worm of the still; *old rum*, on the contrary, rarely contains the poison; a circumstance which affords a good illustration of the action of *tannin* in precipitating the metal in an insoluble form, for Dr. Traill states that the rum intended for immediate consumption is collected at once from the still into glass bottles, while that intended to be kept is received into oak casks.

When *oxide of lead* has to be looked for in liquids containing organic substances, a little nitric acid should be added previous to filtration, in order to redissolve any insoluble compound formed by the salts of lead with albumen and other organic principles, sulphuretted hydrogen is then transmitted through

the clear liquor: if a dark-coloured precipitate is formed, the whole is boiled and the precipitate collected on a filter. It is washed and dried, and then boiled with strong nitric acid, by which the sulphide of lead is wholly or in part converted into nitrate, which being soluble in water is filtered, neutralized by ammonia, and submitted to the general reagents as above. Should it be necessary to examine the insoluble matters, they are to be cut in small pieces and incinerated in a crucible with four parts of black flux; any lead that may be present will be found fused into a small button at the bottom of the crucible, and may be removed from the carbonaceous matters by washing with water. If the metal is in the form of dry oxide, it is readily detected by the blowpipe on charcoal, or by mixing it with paste, spreading the mixture on a piece of card, drying and burning it, when metallic lead is immediately produced.

Poisoning by *carbonate of lead* is very common amongst white-lead manufacturers and painters; the poison finds its way into the system continuously and insidiously in minute quantities, inducing the complaint known as *colica pictorum* and paralysis. Cases of this form of poisoning have not been so frequent in manufactories of white lead since the practice has been adopted of grinding the carbonate in water. Dr. A. T. Thompson considers that the *carbonate* is the only compound of lead which possesses poisonous properties; and that if any other salt in small doses becomes so, it is in consequence of its conversion into carbonate in the body. This opinion is not, however, adopted by Dr. Christison, or by Dr. Alfred Taylor. Carbonate of lead is known by the following properties:—(1) it is blackened by sulphuretted hydrogen;—(2) it is soluble with effervescence in nitric acid; if however, as is frequently the case with the commercial carbonate, it contains sulphate of lead or sulphate of baryta, the two latter substances remain undissolved by the nitric acid; the presence of oxide of lead in the nitric acid solution is proved by the tests mentioned above; (3) it is decomposed when ignited on platinum foil, leaving oxide of lead of a yellow colour; (4) it is reduced on charcoal by the blowpipe, metallic lead being produced.

51. *Action of Water on Lead.*

Gmelin, in his elaborate 'Handbook of Chemistry,' sums up the state of our knowledge of the circumstances under which

water becomes impregnated with lead, thus:—1. Clean lead, in contact with water and air, free from carbonic acid, yields a solution of oxide of lead, which turns reddened litmus-paper blue, is turned brown by sulphuretted hydrogen, and gives a white precipitate with sulphuric acid. 2. Water, freed from air by boiling, does not dissolve lead when kept in contact with it in a close vessel. 3. Water which has been agitated with air takes up, in two hours, a quantity of oxide of lead amounting to between $\frac{1}{12000}$ and $\frac{1}{10000}$; it then reddens blue litmus-paper, and gives a brownish-black precipitate with sulphuretted hydrogen. 4. *Spring* water, containing $1\frac{1}{4}$ grains of saline matter in two pints, and no carbonic acid, when passed through a leaden tube 150 feet long, dissolves a quantity of lead sufficient to give a brown colour with sulphuretted hydrogen. 5. *Distilled* water, in contact with lead and air, free from carbonic acid, dissolves $\frac{1}{10000}$ of oxide, acquires an alkaline reaction, and becomes turbid on exposure to the air. Morveau was the first to notice that the presence of small quantities of carbonic acid, sulphuric acid, or of various salts, either prevents or greatly diminishes the quantity of oxide of lead dissolved; and Yorke found that when clean lead was exposed to *spring* water, 10 pounds of which contained 1·21 grain of chloride of sodium and chloride of calcium together with 6·4 grains of carbonate of lime, a slight deposit of brown oxide took place on the surface of the metal, but no oxide was dissolved. In relation to the important subject of the contamination of water by lead, Christison remarks: "Leaden pipes should not be used for conducting water, unless lead remains untarnished after twenty-four hours' immersion; they are unfit for the purpose if the water contains less than $\frac{1}{8000}$th of its weight of salts. If the quantity of salts exceeds this limit, and the salts consist mainly of sulphates and carbonates, leaden pipes may be used; but if they consist chiefly of chlorides, even 1 part in 4000 is not sufficient to prevent the solution of the lead." That it is dangerous, however, to rely on the "preservative action" of sulphates and carbonates, even when the water contains such salts in considerable quantities, will be evident from the following analysis, made by the author, of a water, the action of which on the leaden cistern was so great that the bottom of the vessel was, after six months, eaten into holes. One gallon of this water contained nearly 78 grains of solid matter, the composition of which was—

Silica	0·24
Carbonate of lime	15·09
Carbonate of magnesia	18·97
Sulphate of lime	15·32
Sulphate of potassa	6·79
Sulphate of soda	10·77
Chloride of sodium	11·46
Organic matters	4·10
	77·74

If the organic matters dissolved in water contain nitrogen, *nitric acid* may be formed by the oxidation of that element, which may be greatly promoted by the presence of alkaline carbonates. Water impregnated with nitrates acts powerfully on lead, and if carbonates and sulphates are not also present, the water may hold in solution a very injurious quantity of lead salt. This is illustrated by the following analysis, made by the author, of a well-water from Highgate, in 1848, which acted strongly on the leaden cistern in which it was stored. An imperial gallon contained—

Silica	0·896
Sulphate of potash	17·044
Sulphate of soda	9·515
Chloride of calcium	5·920
Chloride of sodium	9·632
Nitrate of lime	40·120
Nitrate of magnesia	17·064
Organic matters	none
	100·191

In their chemical report on the supply of water to the metropolis, addressed to the Secretary of State, in June, 1851, Professors Graham, Miller, and Hofmann give the following as the most practical conclusions which they arrived at after a long inquiry, undertaken to illustrate the action of water on lead,—a subject, they observe, of great difficulty, and still far from being exhausted:—

Certain salts, particularly sulphates, to which a protecting effect is usually ascribed, did not appear to exercise uniformly that useful property. Some salts, on the other hand, such as chlorides, and more particularly *nitrates*, increase the solvent action of water. Of all protecting actions, that of carbonate

of lime, dissolved in carbonic acid, appeared to be the most considerable and surest. The soluble oxide of lead is converted into the carbonate, which, although not absolutely insoluble, appears to be the least soluble of all the salts of lead. Pure water did not dissolve a quantity of carbonate of lead greater than $\frac{1}{60}$ of a grain to the gallon; while water, on the other hand, which contained already so much as 6 grains of lead to the gallon, had the quantity reduced to $\frac{1}{37}$ of a grain by free exposure to the atmosphere for twenty-four hours, the lead being deposited as carbonate by the absorption of carbonic acid. Carbonic acid is usually present in well, river, and lake waters, in quantity sufficient for protection; and the immunity of such waters from lead impregnation is probably to be ascribed more often to their carbonic acid than to the salts which they may also contain. *Organic* matter in *soft* water is doubly dangerous, as the rapid corrosion which it occasions may be followed by solution of the lead salt formed. As an illustration of the action of soft water, nearly free from earthy carbonates, on lead, even when no soluble organic matter is present, I may refer to a well-water from Hatton, which was analysed by the author, at the request of the Lord Chief Baron, in consequence of its destructive action on the leaden cistern. This water contained 38·47 grains of saline matter per imperial gallon, consisting of—

Carbonate of lime	2·120
Carbonate of magnesia	·880
Carbonate of soda	15·196
Sulphate of potassa	traces
Sulphate of soda	10·456
Chloride of sodium	9·288
Protocarbonate of iron	·480
Silica	·050
	38·470

52. *Recognition and Quantitative Estimation of Lead in Water.*

This, fortunately, is attended with no difficulties, though certain precautions are necessary when the water contains (as almost all natural waters do, more or less) soluble organic matter. We possess, in *sulphuretted hydrogen*, a test, by which the presence of $\frac{1}{4}$ of a grain of lead is indicated in one gallon of distilled water by the production of a brown tinge. In

making the experiment, the beaker should be placed on a sheet of white paper, and a second beaker, to which no sulphuretted hydrogen has been added, should be placed by its side, also on white paper, so that the faintest brown tinge may be rendered evident by comparison; a few drops of pure hydrochloric acid should be added previous to the application of the test. Dr. Smith, in his investigation of the action of the waters of the Dee and the Don on lead pipes and cisterns, employed the tint produced by sulphuretted hydrogen as a means of estimating, quantitatively, the amount of lead deposited in water. 1·6 grains of nitrate of lead were dissolved in 1000 grains of distilled water; a solution was thus prepared, 1000 grains of which contained 1 grain of metallic lead. From an accurately graduated measure, this solution was dropped into a gallon of water containing no lead, until a transmission of sulphuretted hydrogen, the same depth of tint, was developed as in the particular case on trial. Very accurate results are said to have been obtained, until the quantity of lead exceeds $\frac{1}{4}$ grain per gallon, when the colour gets so dark that slight differences cannot be discriminated: $\frac{1}{100}$ of a grain of lead to a gallon of pure water gave a tint quite perceptible, that is, one of metallic lead in *seven millions*, and a less quantity could readily be distinguished by careful comparison, even in specimens previously containing a considerable proportion of lead, the difference of $\frac{1}{100}$th of a grain was plainly visible. The presence of organic matter in solution in water interferes materially with the action of sulphuretted hydrogen on the lead which it may contain; and, as Dr. Smith informs us that nearly one-half of the solid matter in the water of the river Dee consisted of organic matter, it would appear that the method he describes could not give very reliable quantitative results. Previous to applying the sulphuretted hydrogen test, the water should be carefully evaporated to dryness and the residue ignited in a small porcelain capsule, whereby the organic matter is destroyed. The saline matter should be moistened with nitric acid, and then warmed with the addition of acetic acid and water, and, if necessary, filtered. To estimate the amount of lead *quantitatively*, a gallon of the water should be employed; it should be gently evaporated to dryness, and the residue having been moistened with a few drops of nitric acid and ignited, is digested with dilute hydrochloric acid and filtered. The solution is neutralised with carbonate of soda, and acidified with acetic acid; a

small quantity of bichromate of potash is then added, and the liquid set aside for some hours. If a yellow precipitate forms, it is *chromate of lead*, which is redissolved in hydrochloric acid, and tartaric acid and excess of ammonia having been added, sulphuretted hydrogen is passed through the solution. The precipitated sulphide of lead is washed by decantation, and converted into sulphate by evaporating it to dryness with a little fuming nitric acid and a drop or two of sulphuric acid. The ignited residue contains 73·6 per cent. of oxide of lead.

According to Taylor, *sulphuric acid* fails to detect $\frac{1}{15}$ of a grain of acetate of lead in 1 ounce of water, and begins to form a decided precipitate only when the quantity amounts to $\frac{1}{4}$ of a grain. *Iodide of potassium* forms a rich yellow precipitate with soluble salts of lead, which is soluble to some extent in boiling water, separating again, as the solution cools, in the form of magnificent golden-coloured shining plates; it fails, however, according to Taylor, to indicate the presence of $\frac{1}{2}$ a grain of lead in 12 ounces of water.

53. Oxide of Silver. (AgO.)

General characters.—As obtained by dropping solution of nitrate of silver into *caustic potassa*, it is a greyish-brown powder; but, if the solutions are concentrated and boiling, the oxide precipitates as a heavy black powder. Exposed to the rays of the sun, it disengages a certain quantity of oxygen, and turns black. It is entirely reduced by ignition. It is slightly soluble in pure water, and in water of barytes. It reacts alkaline to test paper, and displaces from their combinations with the alkalies a portion of the acids, with which it forms insoluble compounds. It combines with caustic ammonia, giving rise to a dangerous substance (fulminating silver). It readily dissolves in nitric and other acids.

Comportment of solutions of Salts of Silver with reagents.

(Solution of Nitrate of Silver may be used.)

Potassa and *ammonia* produce a light brown precipitate, readily soluble in ammonia (AgO,HO).

The carbonated alkalies produce a white precipitate, soluble in carbonate of ammonia (AgO,CO_2).

Phosphate of soda produces, in neutral solutions, a yellow precipitate, soluble in ammonia ($3AgO,PO_5$). Solution of

ignited phosphate of soda ($2NaO,PO_5$) gives a white precipitate ($2AgO,PO_5$).

Ferrocyanide of potassium gives a white precipitate.

Ferridcyanide of potassium produces a reddish-brown precipitate.

Chromate of potassa produces a rich brown precipitate.

Protosulphate of iron produces a white precipitate, consisting of metallic silver.

Hydrochloric acid and *the soluble chlorides* produce a white curdy precipitate even in exceedingly dilute solutions. This precipitate becomes violet, and finally black, without, however, suffering decomposition by exposure to light. It is insoluble in dilute acids, but readily soluble in ammonia. When heated it fuses, without decomposition, into a horny mass. If the solution of silver be exceedingly dilute, hydrochloric acid produces an opalescent appearance.

A bar of metallic zinc precipitates silver from its solution in the metallic state.

Hydrosulphuric acid produces a black precipitate, both in acid and in neutral solutions. (AgS.)

Sulphide of ammonium gives a black precipitate, insoluble in excess.

Before the blowpipe, mixed with carbonate of soda, and heated on charcoal, salts of silver are readily reduced, while no incrustation takes place.

Characteristic reaction.—That with hydrochloric acid.

54. Suboxide of Mercury. (Hg_2O.)

General characters.—It is a black powder which a very gentle heat converts into metallic mercury and oxide of mercury, and a stronger heat into mercury and oxygen gas. The black powder obtained by the long-continued agitation of the metal, and which was supposed to consist of this oxide, is probably only the metal in a state of very fine division. The soluble salts of this oxide redden litmus-paper, and are decomposed, when mixed with much water, into soluble *acid*, and insoluble *basic* salts.

Comportment of solutions of Salts of Suboxide of Mercury with reagents.

(Solution of Nitrate of Suboxide of Mercury may be used.)

Potassa and ammonia produce a black precipitate insoluble in excess (Hg_2O,HO).

Alkaline carbonates produce a dirty-yellow precipitate which turns black by boiling.

Phosphate of soda produces a white precipitate.

Ferrocyanide of potassium produces a white gelatinous precipitate.

Ferridcyanide of potassium gives a reddish-brown precipitate, which gradually becomes white.

Iodide of potassium produces a greenish-yellow precipitate, soluble in excess. (Hg_2I.)

Chromate of potassa produces a red precipitate.

Hydrosulphuric acid produces a black precipitate, both in acid and neutral solutions. (Hg_2S.)

Sulphide of ammonium produces a black precipitate, insoluble in excess, but decomposed by *potassa* into *sulphide of mercury* and *metallic mercury*. It is not decomposed or dissolved by boiling nitric acid, but easily by aqua regia.

A bar of metallic zinc throws down an amalgam of zinc and mercury.

Hydrochloric acid and *soluble chlorides* produce a white precipitate (Hg_2Cl), insoluble in acids, but rendered black by potassa and ammonia, the suboxide being formed.

Protochloride of tin produces a grey precipitate, which, boiling, resolves into globules of metallic mercury. A drop of solution of a salt of suboxide of mercury, rubbed with a rag on a piece of bright copper, leaves a silvery stain, which disappears when it is heated to redness.

Before the blowpipe, mixed with carbonate of soda, and heated in a glass tube, metallic mercury sublimes in the form of a grey powder, which, on being rubbed with a glass rod, is resolved into globules. Calomel (Hg_2Cl) should be used for this experiment.

Characteristic reactions.—Those with *hydrochloric acid, potassa*, and *ammonia*.

55. Oxide of Mercury. (HgO.)

General characters.—It is a brick-red crystalline powder; but when finely pulverized has a yellow tinge. At a slightly elevated temperature it turns black, but it regains its red colour on cooling. At a red heat it is resolved into oxygen gas and metallic mercury, and is entirely volatilized. In this manner the presence of impurities, red-lead or brick-dust, may be detected. It dissolves readily in acids, but is not acted on by ammonia.

Comportment of solutions of Salts of Oxide of Mercury with reagents.

(Solution of Corrosive Sublimate ($HgCl$) may be used.)

Potassa produces a yellow precipitate (HgO, HO) insoluble in excess. If an insufficient quantity of the alkali be added, the precipitate is reddish-brown. The presence of ammoniacal salts causes the formation of a white precipitate, which is a compound of *amidide of mercury* with undecomposed mercury salts. Thus:

$$2HgCl + NH_3 = (HgNH_2HgCl) + HCl.$$

Fixed carbonated alkalies produce a reddish-brown precipitate, insoluble in excess, but converted, in the presence of ammoniacal salts, into the above white product.

Carbonate of ammonia produces a white precipitate.

Phosphate of soda produces a white precipitate.

Ferrocyanide of potassium produces a white precipitate, which eventually becomes blue.

Ferridcyanide of potassium produces, in solutions of the nitrate and sulphate, a yellow precipitate; in solutions of the chloride, *none.*

Hydrosulphuric acid and *sulphide of ammonium* give rise to different-coloured precipitates according to the quantity of the reagent added. If it be added in small quantity, and the solution agitated, the precipitate is white, being a compound of sulphide of mercury and undecomposed salt; the addition of larger quantities causes the precipitate to assume, successively, a yellow, orange, brown, red, and black colour. (HgS.) The sulphide of mercury is soluble in solution of potassa, but not in boiling nitric acid, though it dissolves readily in aqua regia.

Iodide of potassium produces a cinnabar-red precipitate, soluble in excess. (HgI.) It crystallizes out of a hot solution in magnificent crimson spangles.

Protochloride of tin added in small quantity to a solution of chloride of mercury, gives rise to the precipitation of subchloride.

$$2HgCl + SnCl = Hg_2Cl + SnCl_2.$$

When the reagent is added in excess, the subchloride is in its turn decomposed, a grey powder being formed, which may, by boiling with a few drops of hydrochloric acid, be united into globules of metallic mercury.

$$Hg_2Cl + SnCl = Hg_2 + SnCl_2.$$

The Galvanic Tests.—On placing a drop of a strong solution of

corrosive sublimate on a gold coin, and touching the latter through the solution with an iron point, the mercury will be deposited on the coin in the form of a bright silvery stain. This elegant test has been modified in a variety of ways. By the following process of Deverge distinct indications are obtained where the poison does not form more than an 80,000th part of the water. A thin plate of gold, and another of tin, a few lines broad, and two or three inches long, are closely applied to one another by silk threads at the ends, and then twisted spirally; this small galvanic pile is left for twenty-four or twenty-six hours in the solution previously acidified with hydrochloric acid, upon which the gold is found whitened, and mercury may be obtained in globules by heating the gold in a tube. For facility of application, an important condition is, that the quantity of fluid should not exceed three or four ounces, because, in a larger quantity, a pile of the size stated cannot remove the whole of the mercury.

Characteristic reactions.—Those with *potassa* and *ammonia.*

56. *Poisoning by Mercury. Detection of the Metal in Organic Mixtures.*

From the researches of M. Boullay and Professor Orfila, it appears that various vegetable fluids, extracts, etc., possess the power of decomposing corrosive sublimate, a portion of the chlorine being gradually disengaged in the form of hydrochloric acid; the salt is consequently converted into calomel, which is deposited in a state of mixture, or combination with vegetable matter. It has been further shown by Professor Taddei, of Florence, that *gluten* possesses the same property in a remarkable degree, and that that vegetable principle is capable of removing the poison completely from its solution, forming with it a ternary compound of *protochloride of mercury* and *gluten.* Among soluble vegetable principles, *albumen, casein,* and *gelatin* possess similar properties; hence solution of albumen is an antidote against the effects of the poison. Various *insoluble* animal principles have been likewise shown to act on corrosive sublimate in the same manner as vegetable gluten, and this chemical action appears to be the source of the corrosive property of the poison. With these facts before us, it is evident that in examining cases of poisoning by corrosive sublimate, we must not always expect to find it in a state of solution, even though it may have been re-

ceived into the stomach in considerable quantities. The attention of the toxicologist must, therefore, be directed to both the liquid and the solid portions.

1. *Examination of the liquid portion.*—It is filtered from the solid matter, and a portion tested with protochloride of tin or by the galvanic test. Should evidence of the poison be thus obtained, the remainder of the solution is mixed with half its volume of ether and well agitated: on allowing it to stand some time, the greater part of the ether rises to the surface, and may be removed by a pipette. It should then be filtered, and evaporated to dryness, or distilled; and the residue, being redissolved in water, is submitted to the proper tests. Dr. Taylor does not find this process to answer unless the poison is present in a moderately large proportion. He therefore recommends to acidulate the suspected fluid with hydrochloric acid, and to immerse in it a narrow slip of finely laminated zinc, round which a spiral slip of fine gold-foil has been twisted: if at the end of five or six hours the gold still retains its bright colour, no corrosive sublimate is present. Should it, on the other hand, be tarnished, it is washed, first in ether, and then in water, dried, and heated in a small reduction tube to obtain a sublimate of the metal.

2. *Examination of the insoluble matters.*—They are boiled with distilled water, and the liquid having been filtered is tested as above described. Should no trace of the poison be thus obtained, Dr. Christison triturates the whole of the insoluble matters with protochloride of tin, and collects and washes the coagulum formed; he then boils it with a moderately strong solution of caustic potassa in a glazed porcelain vessel till all the lumps have disappeared. The animal and vegetable matters, and oxide of tin united with them are thus dissolved, and a powder of metallic mercury, generally easily discernible with a small magnifier, subsides. To separate it, the solution is allowed to remain at rest at a temperature little short of ebullition for fifteen or twenty minutes; the vessel is then filled up with hot water, and the fatty matters which float on the surface skimmed off. After two or three affusions, the black powder is transferred to a smaller vessel, and finally dried, and sublimed in a small tube. By this mode of operating, Dr. Christison has detected a quarter of a grain of corrosive sublimate mixed with two ounces of beef, or with five ounces of new milk, or porter, or tea, made with a liberal allowance of cream and sugar. He has also thus detected a tenth part of a grain

in four ounces of the last mixture, that is in 19,200 times its weight. Dr. Taylor directs that the coagulum obtained by triturating the organic mixture with protochloride of tin should be well boiled in strong hydrochloric acid previous to digesting it with caustic potassa, in order to separate the mercury from the oxide of tin and organic matters, and to estimate it quantitatively. In cases where the quantity of poison is small, he has found this mode of treatment to be troublesome and not unattended with risk. In such cases, he prefers the galvanic test, by which he states that he has detected one-sixteenth part of a grain of corrosive sublimate dissolved in one ounce of organic liquid, and obtained metallic mercury from it in less than half an hour; and he does not think it possible to conceive a case where, in an analysis of this kind, the galvanic test would not be immediately applicable.

In the 'Comptes-Rendus,' March 31, 1845, MM. Danger and Flandin have described their method of extracting mercury from the *liver* of an animal poisoned by corrosive sublimate: the process is nothing more than a modification of the galvanic test, but the experiments are valuable as proving the absorption of the poison. Their process is as follows:—The animal substance finely cut up is heated to about 212°, with one-third or half its weight of strong sulphuric acid; in an hour or two, the whole forms a dark carbonaceous-looking liquid. It is allowed to cool, and chloride of lime gradually added. The liquid becomes whiter and more viscid. The quantity of chloride used is about equal to the weight of the sulphuric acid; it is added until the whole appears like a white calcareous mass. The dried residue is then digested in absolute alcohol, which dissolves the mercurial compound. It is now diluted with water, and the earthy residue repeatedly washed, the liquids being afterwards mixed and concentrated. The concentrated liquid is placed in a funnel terminating at an angle of 90° in a capillary point—the galvanic plates of gold and tin being introduced into the contracted part of the funnel. In this way every drop of the liquid comes in contact with the metals, and the gold is slowly covered with mercury. They state that they have thus detected the metal in a solution containing the 100,000th part. According to Dr. Taylor, it is easy to detect corrosive sublimate in organic solids by simply boiling them with *copper gauze* and a few drops of hydrochloric acid.

It must be observed that Orfila takes an exception to the em-

ployment of tin and gold as the galvanic elements, and on these grounds:—"Some *tin*," he says, "may, after a time, be dissolved, and precipitated on the gold, and thus simulate the appearance of mercury; the whitened gold, when exposed to heat, may even recover its golden colour; the whitening of the gold does not, therefore, absolutely demonstrate the existence of a mercurial compound in the suspected substance; and, if the fluid metal cannot be afterwards obtained in distinct globules, the evidence must be regarded as inconclusive."

When corrosive sublimate is contained in organic substances (albumen, etc.), insoluble in water, Rose recommends to digest them in *ammonia* in preference to *potassa*, the mercury being subsequently precipitated on copper much more readily from an ammonical than from a potassa solution; and, in cases where ammonia fails to effect a solution, he prefers the following method of treatment to the ordinary one of digesting with nitric acid:—The dried substance mixed with about a quarter of its weight of carbonate of potassa is introduced into a capacious retort, and distilled at a heat gradually increasing to redness: the mercury rises and is condensed in the neck of the retort, where it can easily be distinguished from the brown viscid empyreumatic oil which passes over at the same time. If the organic matter contained only slight traces of mercury, the whole of the metal is found in the neck of the retort, none passing with the oil into the receiver.

57. Teroxide of Bismuth. (BiO_3.)

General characters.—When pure, it is of a straw-yellow colour, and melts at a strong red-heat to an opaque glass, which, while hot, is dark-brown or black, but on cooling becomes yellow; when melted with silica, alumina, or metallic oxides, it dissolves them readily. The oxide precipitated by water retains nitric acid, from which it may be freed by caustic potassa or soda, which convert it into a hydrate. It is easily reduced by ignition with organic substances or charcoal powder. Its salts are colourless.

Comportment of solutions of Salts of Bismuth with reagents.

(Solution of Nitrate of Teroxide of Bismuth may be used.)

Potassa and *ammonia* produce white precipitates, insoluble in excess.

Alkaline carbonates and *phosphate of soda* produce white precipitates.

Ferrocyanide of potassium occasions a white precipitate, insoluble in hydrochloric acid.

Ferridcyanide of potassium produces a light yellow precipitate, soluble in hydrochloric acid.

Iodide of potassium produces a brown precipitate, readily soluble in excess.

Chromate of potassa produces a yellow precipitate, soluble in dilute nitric acid.

Hydrosulphuric acid and *sulphide of ammonium* produce a black precipitate both in acid and neutral solutions, insoluble in excess, and in dilute nitric acid, but soluble in boiling nitric acid. (BiS_3.)

Before the blowpipe, heated on charcoal in the reducing flame, salts of bismuth are easily reduced to brittle globules, which spring to pieces under the hammer; the charcoal at the same time becomes covered with a yellow incrustation.

Characteristic reaction.—The neutral salts of bismuth are distinguished by their property of being decomposed by water into a soluble *acid*, and an insoluble *basic* salt. The chloride of bismuth exhibits this property in the most marked manner. The insoluble basic bismuth salt is distinguished from the basic salt of antimony formed under similar circumstances by its being insoluble in *tartaric acid.*

58. Oxide of Cadmium. (CdO.)

General characters.—The colour of this oxide varies according to its state of aggregation. It is sometimes of a deep red-brown, sometimes clear brown, and occasionally black. It is infusible, and does not volatilize at exceedingly high temperatures; but, when mixed with powdered charcoal, it is reduced by heat, and the metal burns and volatilizes. By long-continued gentle ebullition of the metal, the oxide may be obtained, according to Herapath, in long purple needles, opaque, and grouped in rays. Its hydrate is white; it loses its water by heat, and absorbs carbonic acid from the air. It is not soluble in the fixed alkalies, but it dissolves in caustic ammonia. It dissolves easily in acids, forming colourless solutions.

Comportment of solutions of Salts of Cadmium with reagents.

(Solution of Chloride of Cadmium may be used.)

Potassa and *ammonia* produce a white precipitate (HO,CdO), insoluble in potassa, but easily soluble in ammonia.

The carbonated alkalies produce a white precipitate (CdO, CO_2), insoluble in excess: ammoniacal salts do not prevent the formation of this precipitate.

Phosphate of soda produces a white precipitate.

Oxalic acid produces a precipitate soluble in ammonia.

Ferrocyanide of potassium produces a slightly yellow precipitate, soluble in hydrochloric acid.

Ferridcyanide of potassium produces a yellow precipitate, also soluble in hydrochloric acid.

Hydrosulphuric acid and *sulphide of ammonium* produce a rich yellow precipitate (CdS), insoluble in excess, and in dilute acids and alkalies, but decomposed by boiling and concentrated nitric acid.

A bar of metallic zinc precipitates the metal from its solutions in the form of small, glancing, grey-coloured spangles.

Before the blowpipe, heated with carbonate of soda on charcoal, the metal is reduced and volatilizes, leaving a dark yellow-red incrustation.

Characteristic reactions.—Those with *hydrosulphuric acid* and *sulphide of ammonium.*

59. Oxide of Copper. (CuO.)

General characters.—It is pulverulent, and of a black colour; at a high temperature it fuses, and on cooling exhibits a crystalline fracture. By particular management, Becquerel obtained it in the form of fine tetrahedral crystals, having a high metallic lustre. Heated with charcoal, or in contact with organic matter, it is reduced either to metallic copper or to the suboxide. It dissolves easily in acids with the disengagement of heat, and its solutions have mostly a blue or a green colour. Its hydrate is blue; but at the temperature of boiling water it becomes black, a property which interferes with its employment as a pigment. It does not unite in the humid way with the caustic alkalies; but at a red-heat it combines with both alkalies and earths, forming blue or green compounds. Caustic alkalies containing organic matters dissolve it, forming blue or purple compounds.

Comportment of solutions of Salts of Copper with reagents.

(Solution of Sulphate of Copper may be used.)

Potassa produces a voluminous blue precipitate (HO, CuO), which by boiling loses water and becomes black.

Ammonia added in small quantities produces a green basic

salt, which dissolves in excess, forming a fine blue solution. In this solution potassa produces in the cold a blue precipitate, which by boiling becomes black.

Carbonate of potassa produces a greenish-blue precipitate of basic carbonate of copper, which by boiling is converted into black oxide.

Carbonate of ammonia behaves precisely as ammonia.

Phosphate of soda produces a greenish-white precipitate, soluble in ammonia, forming a blue solution.

Ferrocyanide of potassium produces a chocolate-brown precipitate, insoluble in dilute acids, but decomposed by potassa. (Cu_2Cfy.)

Ferridcyanide of potassium produces a yellowish-green precipitate, insoluble in dilute acids.

Cyanide of potassium produces a yellowish-green cyanide, soluble in excess of cyanide of potassium.

Chromate of potassa produces a reddish-brown precipitate, soluble in ammonia, forming an emerald-green solution, soluble also in dilute nitric acid.

Hydrosulphuric acid and *sulphide of ammonium* produce a black precipitate (CuS), slightly soluble in excess of *sulphide of ammonium*, but insoluble in caustic alkalies, and in sulphide of potassium, and in dilute acids. It is readily decomposed by boiling nitric acid, and is completely soluble in cyanide of potassium.

Metallic iron, when introduced into solutions of oxide of copper, becomes covered with a deposit of reduced copper.

Before the blowpipe, salts of copper heated with borax or microcosmic salt in the oxidating flame, gives a grass-green bead, becoming blue on cooling; in the reducing flame the glass is red and opaque; mixed with carbonate of soda, and heated on charcoal in the inner flame the metal is reduced, and gives a bead of metallic copper.

Characteristic reactions.—Those with *ammonia* and *ferrocyanide of potassium*. Solutions of salts of *sesquioxide of uranium* produce a chocolate-brown precipitate with ferrocyanide of potassium; but they are at once distinguished from salts of copper by their comportment with ammonia.

60. *Poisoning by Salts of Copper, and detection of the Metal in Organic Mixtures.*

It was long ago shown by Orfila that albumen, milk, tea;

coffee, etc., possess the property of decomposing solutions of the salts of copper, throwing down the oxide in union with various proximate principles. He also found that red wine, bile, vomited matters, and the tissues composing the stomach, although they do not decompose the soluble copper salts, alter materially the action of reagents on them. The following method, however, is applicable to all cases. If the suspected substance be a liquid, it is filtered, and, as a trial test, a clean needle is suspended in it, and allowed to remain for some hours; if, at the expiration of that time, no red coating should be deposited on it, it is certain that no detectable quantity of the poison is present. That the presence of a large quantity of organic matter does not interfere with the action of this simple test, is proved by the following experiment of Dr. Taylor. He dissolved one-third of a grain of sulphate of copper in water, and mixed the solution with four ounces of thick gruel. Ammonia produced no effect on this liquid, and ferrocyanide of potassium gave only a faint reddish-brown discoloration. Two drops of diluted sulphuric acid were added, and a bright needle suspended in the liquid by a thread: in twenty-four hours the needle was covered with a distinct film of copper. The quantity of copper salt here present was less than the 6000th part of the solution. If, then, the needle has indicated copper, a stream of sulphuretted hydrogen is passed through the liquor, and the precipitated sulphide of copper washed, dried, and digested with strong nitric acid, by which it is converted into a mixture of nitrate and sulphate; it is filtered off from the separated sulphur, and the blue solution submitted to the above-mentioned tests for the detection of the metal. If the substance to be examined is too viscid for filtration, Dr. Christison passes it through a muslin sieve, adds two volumes of rectified spirit when cool, and then filters. Another process may be adopted. The filtered liquid is placed in a platinum crucible, dilute sulphuric acid added, and a strip of zinc introduced; wherever the platinum is touched by the zinc, metallic copper is deposited, and after having in this way coated the platinum capsule, the surplus liquid is poured off, and the capsule well washed out; a few drops of nitric acid, with a small quantity of water, may be used to dissolve out the copper. In this way a pure solution of nitrate of copper may be obtained, and the metal, if in moderate quantity, may thus be separated from the most complex organic fluids.

But all these processes may fail to give any proofs of the existence of copper, and yet the poison may be present in a state of intimate union with some organic principles, or with the mucous membrane of the stomach, in which cases it would be insoluble. The following process must then be adopted. The solid substance is cut into small pieces, and added in successive portions to an equal weight of nitric acid; the mixture is then heated in a porcelain basin, with a fifteenth part of chlorate of potassa. After the whole has been added, the product is heated till it becomes dark-red and thick. The charring being complete, the carbonaceous mass is pulverized, then boiled with nitric acid diluted with its own volume of water, evaporated to dryness, redissolved, and the clear filtered solution tested with reagents. It must be mentioned, however, that objections have been raised against this mode of treatment, or rather against the conclusions that might be drawn from them, on the ground that copper exists *naturally* as a constituent part of many animal and vegetable substances, and more especially in the organs of the human body. Meissner and Sarzeau have examined a great many vegetable substances, and the latter chemist states that he has succeeded in separating metallic copper from *chinchona bark*, *madder*, *coffee*, *wheat*, and *flour*. Devergie, M. O. Henry, and Orfila assert that they have detected traces of copper by the process of incineration, in the bodies of animals not poisoned with the preparations of that metal. Chevreul, on the other hand, could detect no traces of copper in beef, veal, or mutton, and more recently MM. Danger and Flandin have positively denied that copper is ever found naturally in the human body. An extensive inquiry into this subject was undertaken by M. Boutigny, who thinks that he has traced the presence of copper in vegetable substances to its existence in the manures used for raising the different crops, and in animal substances either to their having been preserved or prepared in copper vessels, or to the animals having been fed on vegetables which had received a cupreous impregnation from the cause above mentioned. Another chemist traced the copper which made its appearance in his experiments to the filtering-paper he was using. Dr. Taylor remarks, in reference to this subject, that in a practical view the objection amounts to nothing, since there would be very few cases in which all the chemical evidence rested on the incineration of the viscera, abundant proofs of the poison being generally afforded by an analysis of

the contents of the stomach; the normal copper said to exist in food has not been found to form more than the 100,000th part of the food examined; and if the imputation of poisoning were well founded, and copper were discovered at all, the metal would be in infinitely larger proportion, so as to leave no doubt of its actual admixture.

A not unfrequent cause of accidental poisoning by salts of copper arises from the action of certain articles of food on the metal when used for culinary purposes. Pure water may be kept for any length of time in a clean copper vessel, without becoming in the least impregnated with the metal, provided the air be excluded; if, however, air has access, a hydrated carbonate, mixed with oxide of copper, is gradually formed. If the water contain common salt, or various other saline matters, it is found to exert a greater or less action on the metal, and to become impregnated with it. It appears, however, from the experiments of Falconer and Eller, that neither milk, tea, coffee, beer, cabbage, potatoes, and sundry other vegetables exert the least action on clean copper vessels, even by long boiling; but, if the vessel be not thoroughly clean, all acid substances dissolve the carbonate that encrusts it, especially if left in it for some time. Oily and fatty matters, also, if left for some time in copper vessels, become contaminated to such an extent as to acquire a nauseous coppery taste and a distinct green colour.

It was observed by Dr. Falconer that syrup of lemons might be boiled for fifteen minutes, in copper or brass pans, without acquiring any sensible impregnation; but if it was allowed to cool, and remain in the pans for twenty-four hours, the impregnation was discoverable by the test of metallic iron, and was perceptible to the taste. Proust made the same observations with regard to food prepared in copper vessels; and Dr. Christison quotes a fatal accident which occurred from a servant having left some sour-krout for only a couple of hours in a copper vessel which had lost the tinning. As a general rule, no articles of food which contain saline, acid, or oily principles, should be prepared in copper vessels. Vinegar is occasionally found to contain traces of copper; and it is a well-known fact that sulphate of copper is sometimes employed for the purpose of giving a rich green colour to preserved fruits and vegetable pickles; the presence of the poisonous metal is easily detected by the iron test. In many old cookery books, halfpence are directed to be put amongst the pickles, to give them a fine

green colour. In order to prevent accidental impregnations, copper vessels employed in cookery are coated with an alloy of tin and lead; there is no danger to be apprehended from the latter metal, for, although some of its salts are poisonous, it has been ascertained that the substances which possess the property of dissolving lead cannot attack that metal before the whole of the *tin* in the alloy is oxidated. Sulphate of copper was, some years ago, extensively employed in France by bakers, who used it to accelerate the panary fermentation; the proportion required being an ounce of the salt in two pints of water for every hundredweight of dough. Some chemists have denied that sulphate of copper possesses any such property as that imputed to it by the French bakers; but, from the experiments of Meylink, it appears that not only does the fermentation of the dough take place more quickly, but that the adulterated loaves, when taken out of the oven, are much whiter and much better raised than those not adulterated; he found that, if more than eight grains of the salt were added to half a Flemish pound of dough, it could be detected by a peculiar taste and a slight green colour. He found, moreover, that the employment of the salt of copper, even in the small proportion of one grain, had the singular effect of bringing about the complete fermentation of the dough with considerably less loss of weight than occurs in the common process of baking; the loss in the sound and in the adulterated loaves being in the proportion of 116 to 100. These remarkable results appear to require confirmation; but, if they are correct, the object of the French bakers in employing sulphate of copper is easily explained, the practice being a fraud on the public, by enabling them to make their loaves of a standard weight with a less allowance of nutritive material. It does not appear that this practice has extended to England. A case of poisoning by copper, from the use of German silver, which contains fifty per cent. of copper, is mentioned by Dr. Taylor. It appears that a spoon made of this material had been left in an earthenware vessel in which eels had been cooked with butter and vinegar; and chemical analysis showed that the cupreous poison had thereby been introduced.

61. Oxide of Palladium. (PdO.)

General characters.—It is a black powder, acted upon with great difficulty by acids. The hydrate is of a deep brown co-

lour, and parts with its water only at a high temperature. Its solution in nitric and nitro-hydrochloric acid has a red-brown colour.

Comportment of solutions of Salts of Palladium with reagents.

(Solution of Chloride of Palladium may be used.)

Potassa precipitates a yellowish-brown basic salt, soluble in excess.

Ammonia precipitates from solution of chloride of palladium a compound of chloride of palladium and ammonia ($PdCl, NH_3$), soluble in excess of ammonia.

Carbonated alkalies precipitate a yellowish-brown basic salt, soluble in excess of the precipitants.

Cyanide of potassium and *cyanide of mercury* produce a yellowish-white precipitate of cyanide of palladium, soluble in great excess of hydrochloric acid.

Hydrosulphuric acid and *sulphide of ammonium* produce a black precipitate, insoluble in sulphide of ammonium.

Protochloride of tin produces a black precipitate, soluble in hydrochloric acid, forming an intense green solution.

Palladium salts are reduced by *sulphurous acid*, and by being heated with a salt of *oxide of iron*, or with a *formiate*.

Characteristic reactions.—Those with *cyanide of potassium, cyanide of mercury*, and *protochloride of tin*.

62. SESQUIOXIDE OF RHODIUM. (R_2O_3.)

General characters.—The metal, as well as the anhydrous sesquioxide, is insoluble even in boiling *aqua-regia*. Both, however, are dissolved by fusion with *bisulphate of potassa*, or on heating a mixture of both with chloride of sodium to redness and passing over it a stream of chlorine. The colour of the hydrated oxide is greenish-grey. The haloid salts of this metal are red: the oxysalts yellow, red, or brown.

Comportment of Salts of Sesquioxide of Rhodium with reagents.

Potassa does not occasion any immediate precipitate; but after protracted digestion a precipitate of a greenish-yellow colour makes its appearance, soluble in excess of the precipitant.

Ammonia and *carbonate of ammonia* produce, after a time, a yellow precipitate, composed of sesquioxide of rhodium and ammonia, which is soluble in hydrochloric acid.

Iodide of potassium throws down yellow iodide of rhodium.

Hydrosulphuric acid and *sulphide of ammonium* produce, after a time, a dark-brown precipitate.

All the salts of rhodium are decomposed, and the metal is reduced by exposure to a gentle heat in contact with dry hydrogen gas. They are decomposed also by iron and zinc, which cause a deposit of metallic rhodium.

63. OXIDES OF OSMIUM. (OsO; Os_2O_3; OsO_2; OsO_4.)

The presence of osmium is discovered in its salts by mixing them with a little carbonate of soda, and heating on platinum foil; the metal is converted into osmic acid, which possesses an extremely acrid and penetrating odour like chloride of sulphur, attacking powerfully the olfactory and respiratory organs, and producing, even in minute quantities, a burning sensation in the eyes. It communicates also a considerable brilliancy to flame. The metal itself is whitish, like platinum, but less brilliant. It is easily pulverized. It dissolves in nitric acid and in aqua-regia, osmic acid passing over with the water of the acid. Osmic acid is easily reduced by many metals and organic compounds. Solutions of salts of oxide of osmium are precipitated by *hydrosulphuric acid* and *sulphide of ammonium* as a brownish-black sulphide, insoluble in *sulphide of ammonium.*

General Remarks on the Oxides of the Fifth Group, (Section A.)

The metallic oxides constituting this section admit of a division into two sub-sections by their comportment with hydrochloric acid. Three of them, viz. *oxide of lead, oxide of silver,* and *oxide of mercury,* are precipitated by that reagent; the others are not. Of the chlorides thus formed, *chloride of silver* is easily separated from the other two by ammonia, in which it is perfectly soluble, and from which it is again precipitated by nitric acid. The same alkali decomposes *subchloride of mercury,* converting the metal into black suboxide, from which *chloride of lead* may be removed by boiling water, and the metal tested for in the clear solution by any of the reagents mentioned under its head. The insolubility of sulphide of mercury in nitric acid serves to separate this metal from all the others in the group. The precipitates caused by *potassa* and *ammonia* in solutions of *oxide of cadmium* and *oxide of copper* are soluble in *ammonia;* those of the others are not; but the *hydrated oxide of copper* is soluble also in *carbonate of*

ammonia. *Hydrated oxide of cadmium* has no such property; moreover, the blue colour of the ammoniacal solution of *oxide of copper* is perfectly characteristic of that metal. *Cadmium*, again, is distinguished by the colour of its sulphide, which, being insoluble in *sulphide of ammonium*, distinguishes it from the yellow sulphides of some of the metals in the next group, all of which *are* soluble in *sulphide of ammonium*. *Oxide of bismuth* is readily detected by the decomposition of its salts by water. *Salts of palladium* are recognized by their behaviour with *cyanide of mercury* and *cyanide of potassium*. The insolubility of *oxide of rhodium* in acids, and the colour of its salts, serve to distinguish this metal; and the presence of *osmium compounds* is recognized by the penetrating odour of *osmic acid*.

GROUP V.—Section B.

Metallic oxides precipitated from their acid solutions by Hydrosulphuric Acid, but not from their alkaline solutions, their sulphides being soluble in alkaline sulphides.

(*Antimony, Arsenic, Tin, Platinum, Iridium, Gold, Selenium, Tellurium, Tungsten, Vanadium, Molybdenum.*)

64. Teroxide of Antimony. (SbO_3.)

General characters.—It is a white powder, having a great tendency to assume the crystalline form; by sublimation it is obtained in brilliant, white, prismatic crystals, in which state it is sometimes met with naturally; heated in the air, it burns, emitting a white smoke, and becomes partly converted into *antimonious acid* (SbO_4). Heated in a close vessel, it melts into a yellow liquid, which on cooling becomes nearly white and crystalline; at a higher temperature it sublimes, leaving no residue. It is dissolved in small quantities by boiling water. This oxide is insoluble in nitric acid; but it dissolves in hydrochloric acid, and the solution is decomposed by water, a basic salt being separated, which is readily dissolved by *tartaric acid* and *acetic acids;* and a certain quantity of the oxide is held in solution by the liberated acid.

$$6\,SbCl_3 + 15\,HO = (SbCl_3, 5\,SbO_3) + 15\,HCl.$$

Comportment of solutions of Salts of Teroxide of Antimony with reagents.

(Solution of Sesquichloride of Antimony may be used.)

Potassa and *ammonia* produce white precipitates, soluble in *potassa.*

Alkaline carbonates and *phosphate of soda* behave in a similar manner.

Metallic zinc throws down metallic antimony as a black powder; if nitric acid be present, the sesquioxide is precipitated at the same time.

Hydrosulphuric acid throws down from acid solutions an orange yellow precipitate (SbS_3), readily soluble in excess and in *potassa;* but very sparingly soluble in *ammonia*, and almost entirely insoluble in *carbonate of ammonia.* It is insoluble in dilute acids, but is decomposed by concentrated and boiling hydrochloric acid; the precipitate is very incompletely formed in neutral solutions.

Sulphide of ammonium produces an orange-yellow precipitate, completely soluble in excess.

The solution of double tartrate of antimony and potassa (tartar emetic) is only precipitated after a time by alkalies and their carbonates.

Antimony possesses the property of forming a gaseous combination with hydrogen; the union of these two bodies may be brought about by adding zinc and sulphuric acid to a solution containing the oxide, which becomes deoxidized by the zinc; a portion of the metal unites with the hydrogen of the water, which is at the same time decomposed. *Antimoniuretted hydrogen* is inflammable, burning with a bluish-green flame, and emitting copious fumes of sesquioxide; if the flame be allowed to impinge on a cold surface, such as a porcelain plate, a dark spot of reduced antimony will be produced. If the gas, as it proceeds from an evolution flask, be allowed to pass along a horizontal tube of hard German glass, and the tube be heated to redness at a certain point, decomposition of the gas will take place at that spot, on both sides of which a brilliant mirror of metallic antimony will be deposited: if now a stream of *dry* sulphuretted hydrogen be allowed to pass through the tube, the bright mirror will vanish, and a deposit of a more or less intense yellow colour will take its place, the antimony being converted into *sulphide.* If now the flask in which sulphuretted hydrogen is generating be removed, and its place supplied by

one containing the materials for generating hydrochloric acid gas, and if a gentle stream of this gas be sent through the tube, the yellow deposit will vanish, the *sulphide* being converted into chloride, which being volatile may be conveyed with the gas into a vessel of water, in which the presence of antimony may then be proved by acidulating it with hydrochloric acid, and transmitting through it a stream of sulphuretted hydrogen gas.

Before the blowpipe, mixed with carbonate of soda on charcoal, oxide of antimony is easily reduced, and brilliant metallic globules obtained; the metal fuses and volatilizes, covering the charcoal with a white incrustation, amongst which needle-shaped crystals frequently appear.

Characteristic reactions.—The orange-coloured precipitate with *hydrosulphuric acid;* the decomposition of neutral salts by water, and the solubility of the precipitate thus produced is *tartaric acid.*

65. *Detection of Antimony in Organic Mixtures.*

When tartar emetic has to be sought for in organic mixtures, it may be necessary to examine the solid as well as the liquid portions, in consequence of the property possessed by certain organic principles, particularly such as contain *tannin*, of forming with oxide of antimony insoluble precipitates. The subject of analysis is acidulated with hydrochloric and tartaric acids, and filtered. As a trial test, a piece of paper may be dipped in the clear liquid, and then immersed in sulphide of ammonium; the production of an orange-red stain indicates antimony. The whole of the filtrate is now treated with sulphuretted hydrogen, and the precipitate, after being well washed, is boiled with strong hydrochloric acid, and the solution mixed with a large quantity of water; the formation of a dense white precipitate is characteristic of antimony (the oxychloride). Should no indication of antimony be obtained from the liquid portion, the solid residuum on the filter must be boiled for some time with a strong solution of tartaric acid, filtered, and treated precisely as above. It may still be necessary to examine the tissues of the body. Orfila directs thus:—The thoroughly dried viscera, etc., are boiled with concentrated nitric acid until dissolved; the mass is then evaporated to dryness and carbonized; the carbonized residue is digested with nitro-muriatic acid, by which all the antimony is converted into chloride; a portion is then examined in Marsh's apparatus for an anti-

monial sublimate, and another portion, after being evaporated to dryness, is moistened with sulphide of ammonium. In this way, Orfila succeeded in obtaining proof that antimony is absorbed; he thus detected it in the liver.

It must be remembered, that as preparations of antimony are used as medicine, it is not the discovery of small quantities of the metal that can be received as a proof of intentional poisoning, as in the case of arsenic. Taylor says that tartar emetic is by no means so poisonous as it is often described to be, and that though in doses of from half an ounce to an ounce, or less, it must be regarded as an irritant poison, it has been administered in doses of 40 grains in twenty-four hours to an adult without occasioning any serious mischief.

66. Arsenious Acid. (AsO_3.)

General characters.—As met with in commerce, this acid is almost completely pure; it is without smell and almost without taste; if kept for some time in contact with the tongue, it induces a slightly bitter taste, which, however, leaves one of sweetness. It sublimes before entering into fusion; but with certain precautions it may be fused in close vessels, and obtained on cooling in the form of a colourless transparent glass. When sublimed in a current of air, it forms fine octahedral crystals. Its vapour is without colour or taste; the odour which accompanies it is due either to the reduction of the metal or to the formation of a lower oxide. This acid has two isomeric modifications, one of which is represented by the *vitreous* and the other by the *milky* variety. The latter was supposed to be merely the result of an admixture of water; but it has been ascertained that the two varieties differ both in their specific gravity and in their chemical properties. The action of water on arsenious acid is materially influenced by circumstances. According to Taylor (Guy's Hospital Reports, iv. 81), hot water, cooling from 212° on the poison in powder, dissolves about $\frac{1}{400}$th part of its weight: this is in the proportion of nearly $1\frac{1}{4}$ grain to about 1 fluid ounce of water. According to the same authority (Taylor on Poisons, second edition, p. 355), water boiled for an hour on the poison and allowed to cool, holds dissolved the 40th part of its weight, or about 11 grains to 1 ounce. Cold water allowed to stand for many hours on the poison does not dissolve more than from the 1000th to the 500th part of its weight; that is, $\frac{1}{2}$ grain to 1 grain of

arsenic to nearly 1 fluid ounce of water. The presence of organic matter in a liquid renders arsenious acid much less soluble. Thus, Taylor found that hot tea with milk and sugar and cold porter did not take up more than about ½ grain to the ounce; while hot coffee and cold brandy did not dissolve more than 1 grain to the fluid ounce. The aqueous solution of the acid reddens paper tinged with infusion of turnsole. Rose has observed that a saturated solution of the vitreous acid in hydrochloric acid deposits on cooling octahedral crystals, during the formation of which flashes of light may be observed in the dark: neither of these phenomena occur with the milky variety. The great diversity of statements made with regard to the solubility of arsenious acid in water, has arisen not only from the difference of the two varieties in this respect, but also probably from the different manner in which the experiments have been made. Arsenious acid dissolves much more readily in acids than in water, and is deposited unaltered on cooling from hot solutions. It forms a class of salts called *arsenites*, all of which are poisonous, though not so eminently so as the acid itself. The best antidote to this poison is *hydrated sesquioxide of iron*, perfectly free from alkali, which has not been dried, but preserved in a gelatinous state saturated with water; arsenious acid forms with this oxide a basic insoluble salt. Perhaps the best method of administering this antidote is in the form of a completely saturated solution of the hydrated sesquioxide in *acetic acid*.

Comportment of Arsenious Acid with reagents.

Hydrosulphuric acid produces in aqueous solutions of arsenious acid a very slow precipitation; but in the presence of free hydrochloric acid an immediate precipitate of *sulpharsenious acid* (AsS_3) of a bright yellow colour is produced. This precipitate is easily soluble in *alkalies*, *alkaline carbonates*, and *alkaline sulphides*; it is also decomposed by boiling nitric acid, though it is nearly insoluble in hydrochloric acid. When fused with an alkaline carbonate and nitre, it is decomposed, the products being arseniated and sulphated alkali. When an alkaline solution of sulpharsenious acid is boiled with oxide of copper, sulphide of copper and arseniated alkali are formed.

When vapours of sulpharsenious acid are passed over ignited lime, sulphide of arsenic, sulphide of calcium, and arseniate of lime are formed with the separation of arsenic.

When sulpharsenious acid is fused with cyanide of potassium, sulphocyanide of potassium is formed and arsenic is set free. $2AsS_3 + 3KCy = 3KCyS_2 + As_2$.

This experiment is best made by introducing a mixture of one part of sulpharsenious acid with ten or twelve parts of a mixture of two parts of dry carbonate of soda and one part of cyanide of potassium into a glass tube, drawn out as shown in Fig. 37, and heated to redness while a current of dry carbonic acid gas is passed over it; the arsenic is deposited on the cold surface of the narrow part of the tube in the form of a shining mirror.

A is a flask containing lumps of marble, provided with a funnel-tube, through which hydrochloric acid is passed for the generation of carbonic acid. B is a smaller flask containing oil

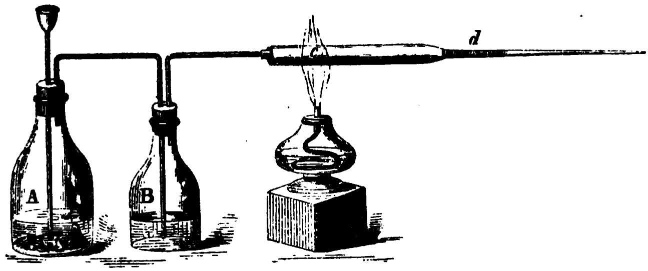

Fig. 37.

of vitriol, in passing through which the carbonic acid becomes dried. The mixture of sulpharsenious acid with cyanide of potassium and carbonate of soda is introduced into the tube *c d* of hard glass so as to occupy about an inch. The dry carbonic acid is allowed to flow slowly for some time through the tube, it is then heated by a spirit lamp, at first gently, and then to a full red-heat, until the mass is completely fused; reduction takes place, and the vapours of metallic arsenic are carried forward and condensed in the narrow part of the tube at *d*, where a *lustrous mirror* or a *grey film* (according to the quantity of arsenic) is deposited. The reduction being complete, the lamp is removed and carbonic acid is allowed to pass slowly through the tube till it is cold. That portion of the tube containing the mirror is then cut off with a file and digested with strong nitric acid, by which it is converted into *arsenic acid;* the

nitric solution is then evaporated till the excess of acid is expelled, a few drops of *nitrate of silver* are added, and then (if necessary) a drop of ammonia, upon which the *brick-red* precipitate characteristic of *arseniate of silver* is obtained.

Arsenious and *sulpharsenious acids* are easily reduced by mixing them with three or four times their weight of *black flux* (obtained by deflagrating equal weights of cream of tartar and nitre in a red-hot earthen crucible) and heating the mixture in a small tube of hard glass. The flux, previously well dried, is well mixed in a mortar with the arsenious or the sulpharsenious acid, and the mixture is introduced into a glass tube about the diameter of a common quill and shaped as in one of the forms indicated in Fig. 38. The gentle heat of a spirit or

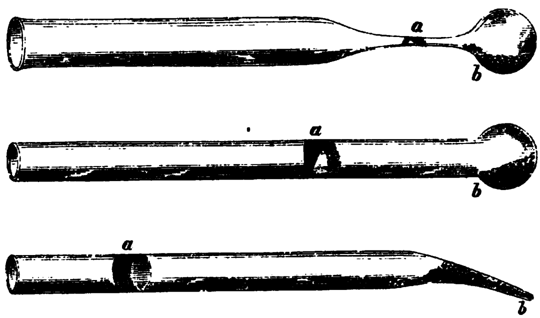

Fig. 38.

gas lamp is applied, and in a short time metallic arsenic will make its appearance on the upper part of the tube, in the form of a brilliant steel-like mirror. Supposing sulpharsenious acid to have been the arsenical compound employed, the following represents the reaction :—

$$AsS_3+3(KO,CO_2)+3C=3KS+3CO_2+3CO+As.$$

When the tube is cold, that portion on which the arsenic is deposited is removed by a file; it is broken up into small fragments, placed in a long, clean, dry test-tube, and heated gently over a gas or spirit lamp, the tube being held in an inclined position; the arsenic becomes oxidized and converted into arsenious acid, which is volatilized and again deposited on the cooler parts of the tube in the form of crystals, which can be readily distinguished as *octahedra* with the aid of a small pocket

lens. When the tube is cold, it is boiled out once or twice with distilled water, which will dissolve the arsenious acid. The solution may be subjected to the following tests:—

Ammonio-nitrate of silver (prepared by adding ammonia to a solution of nitrate of silver in very slight excess, so as nearly but not quite to redissolve the precipitate which is at first formed) produces a *yellow* precipitate ($2AgO,AsO_3$), soluble in ammonia and in dilute nitric acid.

Ammonio-sulphate of copper (prepared by adding a drop or two of ammonia to a solution of sulphate of copper) gives a fine *green* precipitate ($2CuO,AsO_3$), readily soluble in ammonia and in nitric acid.

If a solution of arsenious acid in caustic potassa be warmed with a small quantity of *sulphate of copper*, a red *precipitate* of *suboxide of copper* will be formed, the arsenious acid being converted into arsenic acid.

$$AsO_3+4CuO=AsO_5+2Cu_2O.$$

This, however, is no test for arsenic, since many other substances are capable of reducing protoxide of copper to suboxide.

Arsenic, like *antimony*, forms a gaseous compound with hydrogen. The combination of the two elements may be effected by bringing together *arsenious acid*, or an *arsenite*, with *zinc*, *water*, and *sulphuric* or *hydrochloric* acids. This property is taken advantage of (first by the late Mr. Marsh, of Woolwich) as a test for the metal, and forms a valuable method of isolating it. The materials for generating the hydrogen are introduced into the evolution flask A, Fig. 39, and the gas being dried by passing through a tube filled with dry chloride of calcium B, is inflamed at the point of the bent tube, *c*, (sufficient time being allowed to expel the atmospheric air from the apparatus,) and a porcelain plate depressed on the flame. If, after burning for some time, no incrustation or blackening appears on the plate, it is a sign that the materials in the evolution flask are free from arsenic; additional assurance is, however, obtained by heating a portion of the horizontal tube to redness at *b*, by means of a spirit lamp; no incrustation must be observed in the tube. The liquid to be tested for arsenic is now introduced into the evolution flask through the funnel-tube; and if it contain any traces of the poison, the flame of the hydrogen will acquire a bluish-white colour, owing to the reduction and separation of the arsenic, and fumes of arsenious acid will make their appearance.

lour, and parts with its water only at a high temperature. Its solution in nitric and nitro-hydrochloric acid has a red-brown colour.

Comportment of solutions of Salts of Palladium with reagents.
(Solution of Chloride of Palladium may be used.)

Potassa precipitates a yellowish-brown basic salt, soluble in excess.

Ammonia precipitates from solution of chloride of palladium a compound of chloride of palladium and ammonia ($PdCl, NH_3$), soluble in excess of ammonia.

Carbonated alkalies precipitate a yellowish-brown basic salt, soluble in excess of the precipitants.

Cyanide of potassium and *cyanide of mercury* produce a yellowish-white precipitate of cyanide of palladium, soluble in great excess of hydrochloric acid.

Hydrosulphuric acid and *sulphide of ammonium* produce a black precipitate, insoluble in sulphide of ammonium.

Protochloride of tin produces a black precipitate, soluble in hydrochloric acid, forming an intense green solution.

Palladium salts are reduced by *sulphurous acid*, and by being heated with a salt of *oxide of iron*, or with a *formiate*.

Characteristic reactions.—Those with *cyanide of potassium*, *cyanide of mercury*, and *protochloride of tin.*

62. Sesquioxide of Rhodium. (R_2O_3.)

General characters.—The metal, as well as the anhydrous sesquioxide, is insoluble even in boiling *aqua-regia*. Both, however, are dissolved by fusion with *bisulphate of potassa*, or on heating a mixture of both with chloride of sodium to redness and passing over it a stream of chlorine. The colour of the hydrated oxide is greenish-grey. The haloid salts of this metal are red: the oxysalts yellow, red, or brown.

Comportment of Salts of Sesquioxide of Rhodium with reagents.

Potassa does not occasion any immediate precipitate; but after protracted digestion a precipitate of a greenish-yellow colour makes its appearance, soluble in excess of the precipitant.

Ammonia and *carbonate of ammonia* produce, after a time, a yellow precipitate, composed of sesquioxide of rhodium and ammonia, which is soluble in hydrochloric acid.

Iodide of potassium throws down yellow iodide of rhodium.

Hydrosulphuric acid and *sulphide of ammonium* produce, after a time, a dark-brown precipitate.

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63. OXIDES OF OSMIUM. (OsO; Os_2O_3; OsO_2; OsO_4.)

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The metallic oxides constituting this section admit of a division into two sub-sections by their comportment with hydrochloric acid. Three of them, viz. *oxide of lead*, *oxide of silver*, and *oxide of mercury*, are precipitated by that reagent; the others are not. Of the chlorides thus formed, *chloride of silver* is easily separated from the other two by ammonia, in which it is perfectly soluble, and from which it is again precipitated by nitric acid. The same alkali decomposes *subchloride of mercury*, converting the metal into black suboxide, from which *chloride of lead* may be removed by boiling water, and the metal tested for in the clear solution by any of the reagents mentioned under its head. The insolubility of sulphide of mercury in nitric acid serves to separate this metal from all the others in the group. The precipitates caused by *potassa* and *ammonia* in solutions of *oxide of cadmium* and *oxide of copper* are soluble in *ammonia;* those of the others are not; but the *hydrated oxide of copper* is soluble also in *carbonate of*

lour, and parts with its water only at a high temperature. Its solution in nitric and nitro-hydrochloric acid has a red-brown colour.

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Protochloride of tin produces a black precipitate, soluble in hydrochloric acid, forming an intense green solution.

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General characters.—The metal, as well as the anhydrous sesquioxide, is insoluble even in boiling *aqua-regia*. Both, however, are dissolved by fusion with *bisulphate of potassa*, or on heating a mixture of both with chloride of sodium to redness and passing over it a stream of chlorine. The colour of the hydrated oxide is greenish-grey. The haloid salts of this metal are red: the oxysalts yellow, red, or brown.

Comportment of Salts of Sesquioxide of Rhodium with reagents.

Potassa does not occasion any immediate precipitate; but after protracted digestion a precipitate of a greenish-yellow colour makes its appearance, soluble in excess of the precipitant.

Ammonia and *carbonate of ammonia* produce, after a time, a yellow precipitate, composed of sesquioxide of rhodium and ammonia, which is soluble in hydrochloric acid.

Iodide of potassium throws down yellow iodide of rhodium.

Hydrosulphuric acid and *sulphide of ammonium* produce, after a time, a dark-brown precipitate.

All the salts of rhodium are decomposed, and the metal is reduced by exposure to a gentle heat in contact with dry hydrogen gas. They are decomposed also by iron and zinc, which cause a deposit of metallic rhodium.

63. Oxides of Osmium. (OsO; Os_2O_3; OsO_2; OsO_4.)

The presence of osmium is discovered in its salts by mixing them with a little carbonate of soda, and heating on platinum foil; the metal is converted into osmic acid, which possesses an extremely acrid and penetrating odour like chloride of sulphur, attacking powerfully the olfactory and respiratory organs, and producing, even in minute quantities, a burning sensation in the eyes. It communicates also a considerable brilliancy to flame. The metal itself is whitish, like platinum, but less brilliant. It is easily pulverized. It dissolves in nitric acid and in aqua-regia, osmic acid passing over with the water of the acid. Osmic acid is easily reduced by many metals and organic compounds. Solutions of salts of oxide of osmium are precipitated by *hydrosulphuric acid* and *sulphide of ammonium* as a brownish-black sulphide, insoluble in *sulphide of ammonium*.

General Remarks on the Oxides of the Fifth Group, (Section A.)

The metallic oxides constituting this section admit of a division into two sub-sections by their comportment with hydrochloric acid. Three of them, viz. *oxide of lead*, *oxide of silver*, and *oxide of mercury*, are precipitated by that reagent; the others are not. Of the chlorides thus formed, *chloride of silver* is easily separated from the other two by ammonia, in which it is perfectly soluble, and from which it is again precipitated by nitric acid. The same alkali decomposes *subchloride of mercury*, converting the metal into black suboxide, from which *chloride of lead* may be removed by boiling water, and the metal tested for in the clear solution by any of the reagents mentioned under its head. The insolubility of sulphide of mercury in nitric acid serves to separate this metal from all the others in the group. The precipitates caused by *potassa* and *ammonia* in solutions of *oxide of cadmium* and *oxide of copper* are soluble in *ammonia;* those of the others are not; but the *hydrated oxide of copper* is soluble also in *carbonate of*

lour, and parts with its water only at a high temperature. Its solution in nitric and nitro-hydrochloric acid has a red-brown colour.

Comportment of solutions of Salts of Palladium with reagents.

(Solution of Chloride of Palladium may be used.)

Potassa precipitates a yellowish-brown basic salt, soluble in excess.

Ammonia precipitates from solution of chloride of palladium a compound of chloride of palladium and ammonia ($PdCl, NH_3$), soluble in excess of ammonia.

Carbonated alkalies precipitate a yellowish-brown basic salt, soluble in excess of the precipitants.

Cyanide of potassium and *cyanide of mercury* produce a yellowish-white precipitate of cyanide of palladium, soluble in great excess of hydrochloric acid.

Hydrosulphuric acid and *sulphide of ammonium* produce a black precipitate, insoluble in sulphide of ammonium.

Protochloride of tin produces a black precipitate, soluble in hydrochloric acid, forming an intense green solution.

Palladium salts are reduced by *sulphurous acid*, and by being heated with a salt of *oxide of iron*, or with a *formiate*.

Characteristic reactions.—Those with *cyanide of potassium*, *cyanide of mercury*, and *protochloride of tin*.

62. Sesquioxide of Rhodium. (R_2O_3.)

General characters.—The metal, as well as the anhydrous sesquioxide, is insoluble even in boiling *aqua-regia*. Both, however, are dissolved by fusion with *bisulphate of potassa*, or on heating a mixture of both with chloride of sodium to redness and passing over it a stream of chlorine. The colour of the hydrated oxide is greenish-grey. The haloid salts of this metal are red: the oxysalts yellow, red, or brown.

Comportment of Salts of Sesquioxide of Rhodium with reagents.

Potassa does not occasion any immediate precipitate; but after protracted digestion a precipitate of a greenish-yellow colour makes its appearance, soluble in excess of the precipitant.

Ammonia and *carbonate of ammonia* produce, after a time, a yellow precipitate, composed of sesquioxide of rhodium and ammonia, which is soluble in hydrochloric acid.

Iodide of potassium throws down yellow iodide of rhodium.

Hydrosulphuric acid and *sulphide of ammonium* produce, after a time, a dark-brown precipitate.

All the salts of rhodium are decomposed, and the metal is reduced by exposure to a gentle heat in contact with dry hydrogen gas. They are decomposed also by iron and zinc, which cause a deposit of metallic rhodium.

63. Oxides of Osmium. (OsO; Os_2O_3; OsO_2; OsO_4.)

The presence of osmium is discovered in its salts by mixing them with a little carbonate of soda, and heating on platinum foil; the metal is converted into osmic acid, which possesses an extremely acrid and penetrating odour like chloride of sulphur, attacking powerfully the olfactory and respiratory organs, and producing, even in minute quantities, a burning sensation in the eyes. It communicates also a considerable brilliancy to flame. The metal itself is whitish, like platinum, but less brilliant. It is easily pulverized. It dissolves in nitric acid and in aqua-regia, osmic acid passing over with the water of the acid. Osmic acid is easily reduced by many metals and organic compounds. Solutions of salts of oxide of osmium are precipitated by *hydrosulphuric acid* and *sulphide of ammonium* as a brownish-black sulphide, insoluble in *sulphide of ammonium.*

General Remarks on the Oxides of the Fifth Group, (*Section A.*)

The metallic oxides constituting this section admit of a division into two sub-sections by their comportment with hydrochloric acid. Three of them, viz. *oxide of lead, oxide of silver,* and *oxide of mercury,* are precipitated by that reagent; the others are not. Of the chlorides thus formed, *chloride of silver* is easily separated from the other two by ammonia, in which it is perfectly soluble, and from which it is again precipitated by nitric acid. The same alkali decomposes *subchloride of mercury,* converting the metal into black suboxide, from which *chloride of lead* may be removed by boiling water, and the metal tested for in the clear solution by any of the reagents mentioned under its head. The insolubility of sulphide of mercury in nitric acid serves to separate this metal from all the others in the group. The precipitates caused by *potassa* and *ammonia* in solutions of *oxide of cadmium* and *oxide of copper* are soluble in *ammonia;* those of the others are not; but the *hydrated oxide of copper* is soluble also in *carbonate of*

On now depressing the porcelain plate upon the flame, brown arsenic spots will be obtained: these incrustations have a shining metallic appearance, those of antimony being black and possessing scarcely any metallic lustre. The arsenical crust is, moreover, easily soluble in solution of ***chloride of lime***, that of antimony being unaffected by that reagent. On applying the flame of the spirit lamp to the horizontal part of

Fig. 39.

the tube, an incrustation of metallic arsenic will be formed on the cold part of the tube, which is darker and less silvery than that formed by antimony under similar circumstances; and on cutting off the tube near the deposit and heating it strongly in a long test-tube, the arsenic is converted into arsenious acid, which is recognized by its garlic odour, and which may be dissolved in hot water, and tested by ***nitrate of silver*** and ***sulphate of copper***.

The following modification (Fig. 40) of Marsh's apparatus by the Academy of Sciences of Berlin is described by Dr. Ure (Supplement to the Dictionary of Arts, Manufactures, and Mines):—

B is a narrow glass cylinder open at top, about 10 inches high, and $1\frac{1}{4}$ or $1\frac{1}{2}$ inch in diameter inside. A is a glass tube about 1 inch in diameter outside, drawn to a point at bottom, and shut

with a cork at top. Through the centre of this cork the small tube C passes down air-tight, and is furnished at top with a stopcock, into which the small bent glass tube (without lead) E is cemented. The bent tube E is joined to the end of F by a perforated cork.

This apparatus is used as follows: Introduce a few oblong slips of zinc free from arsenic into A, and then insert its air-tight cork with the attached tubes. Having opened the stopcock, pour into the tube B as much of the suspected liquid, acidulated with dilute pure sulphuric acid, as will rise to the top of the cork in A, and immediately shut the stopcock. The generated hydrogen will force down the liquid out of the lower orifice of A into B, and raise the level of it above the cork. The extremity of the tube F being dipped beneath the surface of a weak solution of nitrate of silver, and a spirit flame being placed a little to the left of the letter E, the stopcock is then to be slightly opened, so that the gas which now fills the tube A may escape so slowly as to pass off in separate small bubbles through the silver solution. By this means the whole of the arsenic contained in the arseniuretted hydrogen will either be deposited in the metallic state upon the inside of the tube E, or a characteristic black powder will be deposited in the silver solution. The first charge of gas in A being expended, the stopcock is to be shut till the liquid be again expelled from it by a fresh disengagement of hydrogen. The ring of metallic arsenic deposited beyond E may be chased onwards by placing a second flame under it, and thereby formed into an oblong, brilliant, steel-like mirror. It is evident that by the patient use of this apparatus, the whole arsenic in any poisonous liquid may be collected, weighed, and subjected to every kind of chemical verification. By means of the perforated cork, the tube F may readily be turned about, and its taper point raised into such a position as, that when the hydrogen issuing from it is

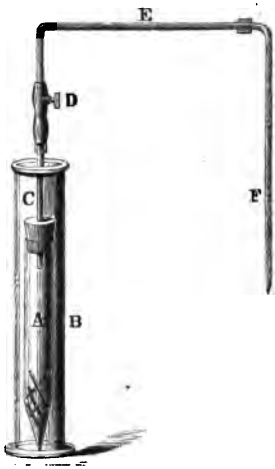

Fig. 40.

kindled, the flame may be made to play upon a surface of glass or porcelain, in order to form the arsenical mirror.

A method of distinguishing between the metallic mirrors formed by antimony and arsenic under similar circumstances, is founded on the decomposition of sulphide of antimony by hydrochloric acid gas and the volatility of the antimony thus formed. We can thus not only distinguish an arsenical from an antimonial deposit, but when both metals are present we can separate them perfectly. We proceed thus:—The mirror having been obtained, a feeble stream of dry sulphuretted hydrogen is sent through the tube, a gentle heat being at the same time applied; if the metal be arsenic alone, sulphide of that metal of a light yellow colour will be formed; if it be antimony alone, the sulphide is either orange-red or nearly black; if both metals be together, then both are converted into sulphides; but the sulphide of arsenic being more volatile than the sulphide of antimony, it will be deposited in a more advanced part of the tube. A current of dry hydrochloric acid gas is now passed through the tube; *chloride of antimony* is formed *without the application of heat*, and is entirely removed in the current of gas. The sulphide of arsenic remains unaltered, and may be distinguished from sulphur by its solubility in ammonia.

Bloxam ('Quarterly Journal of the Chemical Society,' vol. xiii. p. 12), impressed with the difficulties which frequently beset the detection of arsenic by Marsh's process, arising (1) from the occasional presence of the poisonous metal in the zinc and sulphuric acid employed, and (2) by the frothing occasioned by the viscidity of the mixture when organic matters are present, has suggested the employment of the galvanic current. He thus describes his apparatus:—"It consists of a two-ounce narrow-mouthed bottle, the bottom of which had been cut off and replaced by a piece of vegetable parchment tightly stretched over it, and secured by a ligature of fine platinum wire. The bottle is furnished with a cork carrying a small tube, bent at right angles, and connected with the drawn-out reduction-tube by a caoutchouc tube; through this cork passes a platinum wire bent into a hook inside the bottle, for suspending the negative plate. The bottle is placed in a glass of such a size as to leave a small interval between the two, and this glass is allowed to stand in a large vessel of cold water; an ounce of dilute sulphuric acid is introduced into the apparatus, so as to fill the bottle and the outer space to about the same level, the

positive plate being immersed in the acid contained in the outer space. When the bottle has become filled with hydrogen, the shoulder of the reduction-tube is heated to redness during fifteen minutes, to ascertain the purity of the sulphuric acid, and the liquid to be tested is introduced into the bottle by means of a pipette, the cork being removed for an instant (or a tube-funnel may be used); a drachm of alcohol is afterwards added, to prevent frothing." By this process, according to the author, $\frac{1}{100}$ grain and even $\frac{1}{1000}$ grain of arsenious acid can be detected in an organic mixture with the greatest ease and certainty.

Metallic copper (which must be free from arsenic), when boiled with an acidified mixture containing arsenious acid, becomes covered with a steel-grey crust of metallic arsenic. This is an exceedingly delicate test, and will, according to its discoverer, Reinsch, detect the metal when present in no more than ***one-millionth part*** of the liquid; but as various other metals, ***bismuth***, ***antimony***, etc., are likewise precipitated under similar circumstances, it is necessary to submit the crust to a careful examination. The liquid to be tested, having been acidified with hydrochloric acid, is boiled with thin strips or wires of electro-precipitated copper until a distinct film is deposited. The strips or wires are then removed, and thoroughly dried between folds of blotting-paper; they are then introduced into a long narrow test-tube of hard German glass, and carefully heated, in a sloping position, over a spirit or gas-lamp; octahedral crystals (the form of which can be readily recognized with the aid of a small pocket-lens) will soon make their appearance. The tube is allowed to cool, the copper fragments are thrown out, the tube boiled out with distilled water, and the solution tested for arsenious acid with ***sulphuretted hydrogen***, ***ammonio-nitrate of silver***, and ***ammonio-sulphate of copper***. Should oxidizing agents, especially ***chlorate of potassa***, be present in the solution to be tested, no arsenic will be deposited until they are destroyed, but the copper will be dissolved, communicating a blue colour to the liquid. After a time, that is, as soon as the oxidizing agents are removed from the liquor, the arsenic is precipitated upon the undissolved copper. Should that metal itself contain any arsenic, this will also be precipitated; hence the great importance of ascertaining, previous to making the experiment, that the copper is perfectly pure.

Arsenic in paper-hangings.—The paper is cut into strips and boiled for a few minutes with dilute hydrochloric acid, and the filtered liquid treated with metallic copper in the manner described above; or, in order to avoid any ambiguity which may arise from the possible presence of arsenic in the copper or in the hydrochloric acid, a few grains of the suspected green colour may be scraped off and introduced into a clean dry test-tube. The aperture of the tube being closed, it is gently heated in the flame of a gas or spirit-lamp; the green powder soon becomes carbonized, and if arsenic be present a sublimate of arsenious acid is obtained; when cold the carbonized residue is removed, the test-tube is about one-quarter filled with distilled water, a drop or two of solution of caustic potassa added, and the mixture boiled. The solution obtained is tested with ammonio-nitrate of silver, or ammonio-sulphate of copper, when characteristic yellow and green precipitates will be obtained.

67. *Detection of Arsenic in Organic Compounds.*

To prepare an organic mixture suspected to contain arsenic for the reception of sulphuretted hydrogen, Fresenius digests it on a water-bath, with an equal weight of concentrated hydrochloric acid, and as much water as will give the whole a thin consistence; *chlorate of potassa* is then added, in portions of about half a drachm, at intervals of about five minutes, and until the contents of the basin have assumed a bright yellow, perfectly homogeneous, and a thin liquid appearance. When this point is attained, about two drachms more of chlorate of potassa are added to the mixture, and the basin is removed from the water-bath. When cool, it is filtered, and the residue washed, until all acid reaction ceases. The filtrate is concentrated to about a pint, and excess of *sulphurous acid* added, to reduce the *arsenic acid* to *arsenious acid*, the former being far less readily precipitated by sulphuretted hydrogen than the latter. The excess of sulphurous acid is then expelled by heat, and the fluid exposed to a slow stream of sulphuretted hydrogen gas for about twelve hours. The sulphide of arsenic thus obtained, is washed and treated with fuming nitric acid, evaporated to dryness, moistened with pure sulphuric acid, and gently heated, first on the water-bath, and afterwards at a higher temperature (not, however, above 300°), until the mass begins to crumble. The residue is treated with boiling water, filtered, and the limpid fluid, after being acidified with hydro-

chloric acid, is again precipitated by sulphuretted hydrogen. The pure sulphide of arsenic thus obtained is mixed with carbonate of soda and cyanide of potassium, and reduced in an atmosphere of carbonic acid, as above described.

MM. Dufloss and Hirsch proceed as follows:—The suspected mass (the stomach, for instance, with its contents) is digested in a tubulated retort, with an equal weight of pure hydrochloric acid; the retort is connected with a receiver in which a little water is placed, the object of which is to collect any chloride of arsenic that might volatilize during the process. The retort is heated by a bath of chloride of calcium until the mass acquires the consistence of paste, when it is allowed to cool. It is then mixed with twice its weight of strong alcohol, and after some time the undissolved portion is collected on a filter, and washed with alcohol. The alcoholic liquid and the washings are lastly introduced into a retort, and the alcohol distilled off. The residue in the retort is mixed with the acid liquor which passed into the receiver during the first distillation, and the mixture is exposed to sulphuretted hydrogen.

Danger and Flandin heat the organic substance with one-sixth of its weight of concentrated sulphuric acid; the substance is carbonized without foaming; it is continually stirred till the charcoal is dry; a small quantity of nitric acid or aqua-regia is then added, and the whole extracted with water. They observe, however, that the carbonizing process must only be had recourse to when all attempts to obtain evidence of the poison without it, have failed.

Dr. Letheby proposes the following method of treating organic substances, by which he states that it is not difficult to discover $\frac{1}{500}$ of a grain of arsenic in many ounces of organic matter. The substance, if solid, such as the liver, intestine, or muscle, is cut into small pieces and heated to dryness with aqua-regia; the charred mass is boiled with two or three successive portions of water, slightly acidulated with nitric acid, and then boiled for about half an hour with pure granulated zinc, (which is best prepared by exposing to a red-heat, in a Hessian crucible, alternate layers of granulated zinc, and one-fourth of its weight of nitre, taking care to begin by a layer of saltpetre, and to finish by one of zinc; deflagration takes place, and when it is over the scoriæ are removed, and the pure metal run into an ingot), the arsenic will be deposited on the zinc, giving it a greyish-black appearance. The arseniated zinc is

introduced into a Marsh's apparatus of peculiar construction, and the evolved gas conveyed into a jar containing solution of *nitrate of silver*, according to Lassaigne's method; a black precipitate is produced, and by taking the precaution of not allowing the gas to come over too quickly, the whole of it is certain to be decomposed.

$$6(AgO,NO_5)+AsH_3=6Ag+AsO_3+3HO+6NO_5.$$

To this black, turbid solution, hydrochloric acid is added, till all the silver is precipitated, and a little acid remains in excess. It is then boiled for a few minutes, filtered, and evaporated to dryness; the residue, if there be any, is boiled with distilled water, and carefully precipitated by *ammonio-nitrate of silver*. If any arsenic had been present, it would by this process have been converted into arsenic acid, which would give a red precipitate, with ammonio-nitrate of silver.

68. Arsenic Acid. (AsO_5.)

General characters.—This acid, which is even more poisonous than arsenious acid, is remarkable for its analogy with tribasic phosphoric acid. Like the latter, it only partially dissolves in water, leaving a powder, which is only dissolved with great difficulty. At a red-heat it is partially decomposed, and at a high temperature it is resolved into *arsenious acid* and *oxygen*. It is deliquescent, and strongly acid. The salts which it forms are called *arseniates;* they are mostly insoluble or sparingly soluble in water, but dissolve in hydrochloric acid; the alkaline arseniates are soluble in water. *Sulphurous acid*, aided by heat, reduces it into arsenious acid.

Comportment of solutions of Arsenic Acid and the Arseniates with reagents.

Hydrosulphuric acid produces no precipitate in neutral or alkaline solutions; but, in acid solutions, a yellow precipitate (AsS_5) is very slowly formed. Hence, previous to precipitating arsenic, when in the form of arsenic acid, by means of this reagent, it is reduced to arsenious acid by treatment with sulphurous acid.

Nitrate of silver produces a red-brown precipitate of arseniate of silver ($3AgO,AsO_5$), soluble in dilute nitric acid and in ammonia.

Ammonio-nitrate of silver behaves in a similar manner.

Sulphate and *ammonio-sulphate of copper* produce a greenish-blue precipitate ($2CuO,AsO_5$).

Before the blowpipe, heated on charcoal in the inner flame, arseniates are reduced, disengaging the peculiar garlic odour of suboxide of arsenic, by which minute traces may be recognized.

69. Oxide of Tin. (SnO.)

General characters.—When pure, it is black, but by trituration it acquires a grey, green, or brown tinge. It is not altered in dry air, but when brought in contact with bodies in a state of ignition it takes fire, burning with considerable intensity, emitting a white smoke, and is converted into white peroxide (SnO_2). The hydrated oxide, which is obtained by precipitating a solution of the metal in hydrochloric acid by carbonate of potassa, is a white powder, which also takes fire on being brought into contact with a burning body, and glows like tinder. It is more easily soluble than the anhydrous oxide. When boiled in water, it is decomposed and a black powder is formed, which slowly absorbs oxygen, and acquires a lighter colour. Oxide of tin is dissolved by the fixed caustic alkalies. but the solution gradually decomposes, depositing metallic tin, the solution then containing a combination of *peroxide* and alkali. *Chloride* of tin is decomposed when brought into contact with water, an insoluble compound of oxide and chloride being formed. This decomposition is prevented by the addition of free hydrochloric acid.

Comportment of solutions of Oxide of Tin with reagents.

(Solution of Protochloride of Tin may be used.)

Potassa, ammonia, and their *carbonates* produce a white precipitates (SnO,HO), soluble in potassa; by repose, and more rapidly when boiled, the solution is decomposed, *metallic tin* and *peroxide of tin* being formed.

Phosphate of soda produces a white precipitate.

Ferrocyanide of potassium gives a white gelatinous precipitate.

Ferridcyanide of potassium occasions a white precipitate, soluble in hydrochloric acid.

Hydrosulphuric acid and *sulphide of ammonium* produce a dark-brown precipitate, soluble in potassa and in alkaline sulphides, particularly such as contain excess of sulphur; soluble also in hydrochloric acid; but nitric acid converts it by boiling into peroxide of tin; the solution of *sulphide of tin* in *sul-*

phide of calcium is precipitated as a yellow *bisulphide of tin* by hydrochloric acid.

A bar of metallic zinc precipitates tin in small greyish-white metallic spangles.

Chloride of mercury produces a white precipitate of *subchloride of mercury*. (H_2Cl.)

The salts of this oxide, from their tendency to absorb oxygen, are powerful reducing agents; they are all decomposed by exposure to the air, passing into salts of the *peroxide*.

Before the blowpipe, heated in the inner flame on charcoal with a mixture of *carbonate of soda* and *cyanide of potassium*, protosalts of tin yield ductile grains of metallic tin without any incrustation taking place.

Characteristic reaction.—The most characteristic test for protoxide of tin is the reddish-purple coloration or precipitate which its solutions produce with *terchloride of gold.*

70. Peroxide of Tin. (SnO_2.)

General characters.—This oxide differs, according to its mode of formation, not only in its physical, but also in its chemical properties; it is found native and crystallized; the crystals are sometimes yellowish-brown and transparent, and sometimes nearly black: when prepared by the action of nitric acid on the metal, it is a white powder, and almost insoluble in acids, but by fusion with carbonate of potassa it is rendered soluble; the oxide produced by precipitating the perchloride by ammonia is easily soluble in acids; but after it has been ignited it is insoluble, but it is again rendered soluble by fusion with carbonate of potassa.

Comportment of solutions of Peroxide of Tin with reagents.

(Solution of Bichloride of Tin ($SnCl_2$) may be used.)

Potassa and *ammonia* produce a white precipitate, soluble in *potassa* and in great excess of *ammonia*.

Carbonates of potassa and *ammonia* produce a white precipitate, soluble in *carbonate of potassa*, but insoluble in *carbonate of ammonia*.

Phosphate of soda produces a white precipitate.

Hydrosulphuric acid and *sulphide of ammonium* throw down from acid and neutral, but not from alkaline solutions, a yellow precipitate of bisulphide of tin, soluble in alkalies, alkaline carbonates, and sulphides, and in concentrated boiling hydro-

chloric acid; *nitric acid* converts it into peroxide, and by fusion with nitre it gives rise to the formation of *sulphate* and *stannate of potassa.*

A bar of metallic zinc throws down a white gelatinous precipitate, hydrogen gas being disengaged.

Before the blowpipe, heated with carbonate of soda on charcoal in the inner flame, persalts of tin are reduced to the metallic state.

Characteristic reaction.—That with *hydrosulphuric acid.*

71. Binoxide of Platinum. ($Pt O_2$.)

General characters.—The hydrate is obtained as a reddish-brown voluminous precipitate, closely resembling *hydrated sesquioxide of iron,* by precipitating a solution of the nitrate by caustic soda; it contracts considerably on drying; heated in a retort, it loses its water and becomes black; at a higher temperature, it parts with oxygen, leaving the metal. Platinum is insoluble in nitric and hydrochloric acids, but it dissolves in *aqua-regia,* forming a red-brown solution containing bichloride of platinum ($Pt Cl_2$).

Comportment of solutions of Salts of Platinum with reagents.

(Solution of Bichloride of Platinum may be used.)

Potassa produces a yellow crystalline precipitate, consisting of the double chloride of platinum and potassium ($K Cl, Pt Cl_2$); the addition of hydrochloric acid favours its formation; it is insoluble in acids, but dissolves with the aid of heat in *potassa;* it is very slightly soluble in water, and insoluble in strong alcohol.

Ammonia produces a yellow crystalline precipitate, the *double chloride of platinum* and *ammonium* ($N H_4 Cl, Pt Cl_2$) having the same characters as the former, and soluble in excess of ammonia aided by heat; when exposed to a red-heat it is completely decomposed, leaving the metal in a spongy form.

Subnitrate of mercury produces a yellowish-red precipitate.

Chloride of tin communicates to solutions of *bichloride of platinum* a deep red-brown colour, without producing any precipitate.

Hydrosulphuric acid and *sulphide of ammonium,* aided by heat, produce in acid and neutral solutions a brownish-black precipitate ($Pt S_2$), soluble in excess of alkalies and alkaline sulphides, insoluble in nitric and hydrochloric acids, but soluble in aqua-regia.

Characteristic reactions.—Those with *potassa* and *ammonia* in the presence of hydrochloric acid.

72. BINOXIDE OF IRIDIUM. (IrO_2.)

Iridium forms four compounds with oxygen, viz. IrO; Ir_2O_3; IrO_2; IrO_3. Of these, the most important is the *binoxide* (IrO_2). According to Berzelius, (Gmelin,) this oxide is only known in its salts, and cannot be precipitated by alkalies or alkaline carbonates, because they dissolve it; according to Claus, however, it is the most easily prepared of all the oxides of iridium, and is always deposited in the form of a bulky, indigo-coloured precipitate when a solution of either of the chlorides of iridium is boiled with an alkali; this precipitate is a hydrate (IrO_2+2aq). When heated in an atmosphere of carbonic acid it exhibits a strong momentary incandescence, at the same time giving off its water, together with 1 or 1½ per cent. of oxygen, and becoming black and insoluble in acids.

Behaviour of Salts of Binoxide of Iridium with reagents.

Hydrosulphuric acid first decolorizes the solution and then precipitates sulphide of iridium of a brown colour, easily soluble in sulphide of ammonium.

Protochloride of tin decolorizes the solution and forms a pale-brown precipitate.

Protosulphate of iron decolorizes the solution and forms a dirty white or dingy green precipitate.

Subnitrate of mercury produces a pale-brown precipitate.

Oxalic acid and *ferrocyanide of potassium* decolorize the solution.

Ammonia decolorizes the solution and forms a brown precipitate.

Potassa produces a scanty blackish-grey precipitate; the supernatant liquid, which at first is nearly colourless, acquires by standing a violet-blue colour, and yields on evaporation a blue precipitate.

Nitrate of silver produces a deep indigo-coloured precipitate, which after a while becomes colourless.

73. TEROXIDE OF GOLD. (AuO_3.)

General characters.—The hydrate of this oxide, which from its tendency to combine with bases, and from the little disposition which it has to combine with acids, ought perhaps more

correctly to be called *auric acid*, is of a yellowish-red colour; the anhydrous oxide is black or deep-brown. The hydrate, dried without the aid of heat, is of a chestnut-brown colour, and has a vitreous fracture. At 212° it loses its water, and becomes partially reduced; even in the dark it undergoes partial decomposition, and at a red-heat it is resolved into metallic gold and oxygen. The metal is insoluble in nitric or hydrochloric acid, but it dissolves in aqua regia, forming a fine yellow solution, containing terchloride of gold ($AuCl_3$).

Behaviour of solution of Terchloride of Gold with reagents.

Potassa after a time produces an inconsiderable reddish-brown precipitate, consisting of *aurate of potassa* and *chloride of potassium*. $AuCl_3 + 4KO = KO, AuO_3 + 3KCl$.

Ammonia produces a yellow precipitate (aurate of ammonia, or fulminating gold).

Ferrocyanide of potassium communicates to solution of gold an emerald-green colour.

Protosulphate of iron produces in concentrated solutions an immediate dark-brown precipitate of metallic gold.

$$AuCl_3 + 6(FeO, SO_3) = 2(Fe_2O_3, 3SO_3) + Fe_2Cl_3 + Au.$$

In dilute solutions a blue colouring is first perceived, followed by a brown-coloured precipitate.

Protonitrate of mercury occasions a black precipitate.

Oxalic acid produces a precipitate of metallic gold, thus:—

$$AuCl_3 + 3(HO, C_2O_3) = Au + 3HCl + 6CO_2.$$

Protochloride of tin, to which a drop of nitric acid has been added, communicates a reddish-purple colour to very dilute solutions; in concentrated solutions a red-purple precipitate (purple of Cassius) is formed; probably ($AuO, SnO_2 + SnO, SnO_2 + 4aq$) hydrated double stannate of gold and tin.

A bar of metallic zinc precipitates metallic gold in the form of a brown coating.

Hydrosulphuric acid and *sulphide of ammonium* precipitate from neutral and acid solutions of gold, the tersulphide (AuS_3), soluble in great excess of sulphide of ammonium, and in aqua-regia, but insoluble in all other acids and alkalies.

Characteristic reactions.—Those with *protochloride of tin*, *protosulphate of iron*, and *oxalic acid*.

74. Selenious Acid. (SO_2.)

General characters.—On evaporating a solution of selenium

in aqua regia, this acid remains in the form of a white saline mass, which at the temperature of about 600° assumes the form of a deep-yellow gas, much resembling chlorine; on cooling, the acid condenses in long needles, and by allowing it to cool slowly it is deposited in the form of a semitransparent crust. When first prepared it has a brilliant appearance, but by exposure to the air it becomes dull, from the absorption of moisture. Its taste is distinctly acid, but it leaves a burning taste in the mouth; it is very soluble in boiling water: the solution deposits the hydrated acid on cooling in the form of striated prisms. The hydrated acid is also deposited from a hot solution in nitric acid in long prisms resembling nitre. It is easily reduced. On introducing a slip of *zinc* or *polished iron* into a solution of selenious acid mixed with hydrochloric acid, it immediately becomes covered with a copper-coloured deposit, and *selenium* precipitates by degrees in the form of red, brown, or greyish-black flocks, according to the temperature. A mixture of *sulphuric* and *selenious* acids is slowly acted on, and the precipitate contains a little sulphur. Selenious acid is also decomposed by *silver*. *Selenium* is best precipitated from *selenious acid* and the *selenites* by *sulphite of ammonia*. The liquor, which is at first clear, becomes yellow, then turbid, then cinnabar-red, and after a few hours it deposits red flocks of *selenium*. If nitric acid be present, a perfect reduction cannot be effected.

Comportment of Selenious Acid and Selenites with reagents.

Hydrosulphuric acid produces in an acid solution a yellow precipitate of *sulphide of selenium*, which is soluble in *sulphide of ammonium*.

Solid selenites, heated in a tube with *chloride of ammonium*, afford a sublimate of selenium, which is recognized by its peculiar odour.

Before the blowpipe, the minutest trace of selenium may be recognized by ignition on charcoal in the oxidating flame; a strong disagreeable smell, similar to *decaying horseradish*, is given off. If much selenium be present, a reddish vapour is evolved, and a steel-grey sublimate is deposited on the charcoal, which on the exterior edges sometimes passes into violet, and in thin layers blue.

75. Tellurous Acid. (TeO_2.)

General characters.—This acid is obtained in crystalline

grains, by acting on *tellurium* with *nitric acid*, and, as a white flocculent hydrate, by precipitating the solution in nitric acid with water. The yellow colour which the acid frequently exhibits arises from impurities. When first laid on the tongue, it produces little taste; but after a time a very disagreeable metallic taste, similar to that of salts of silver, is experienced. It reddens litmus-paper, though not immediately; it is very sparingly soluble in water. On being heated, it acquires a fine citron-yellow colour; but on cooling it again becomes colourless; at a red-heat it melts into a transparent deep-yellow liquid, solidifying on cooling into a colourless crystalline mass; heated in the open air, it fumes, and slowly sublimes; heated in open vessels with carbon, it is reduced with detonation, the greater part of the tellurium volatilizing; in close vessels the reduction takes place easily, but the metal is obtained with difficulty in a compact mass. It is also reduced, though not very readily, by hydrogen gas. It is very sparingly soluble in *acids*, in *ammonia*, and in the *carbonated alkalies*. The *caustic fixed alkalies*, on the other hand, dissolve it immediately. When *tellurous acid* is fused with an equal weight of *carbonate of potassa*, and the *tellurite of potassa* thus obtained dissolved in water, and mixed with a slight excess of nitric acid, a white voluminous hydrate is produced, which has an acrid metallic taste, instantly reddens litmus-paper, and is soluble in water, and very soluble in nitric and other acids, and also in caustic ammonia and the carbonated alkalies.

Comportment of solution of Tellurous Acid with reagents.

The *caustic alkalies* and their *carbonates* produce a white precipitate, soluble readily in *potassa*, and soluble also in alkaline carbonates.

Hydrosulphuric acid produces a dark-brown precipitate, very soluble in *sulphide of ammonium*.

Sulphurous acid, alkaline sulphites, and *metallic zinc*, produce a black precipitate of metallic *tellurium*.

Protochloride of tin and *protosulphate of iron* produce a black powder, which on being rubbed assumes a metallic lustre.

Before the blowpipe, heated on charcoal, or in a glass tube open at both ends, a white sublimate with a reddish border is obtained in either flame, and which disappears with a beautiful bluish-green tinge; when the reducing flame is directed on it in large quantities, the flame also becomes blue; if the peculiar

smell of horseradish is perceptible, ***selenium*** is present; if the substance under examination contain other metals, as lead or bismuth, it should be mixed with boracic acid, which will dissolve those metals and prevent them from volatilizing.

76. Oxides of Tungsten. (WO_2; WO_3.)

Binoxide of Tungsten.—General characters: This oxide, when prepared by reducing *tungstic acid* by hydrogen gas, is brown; it may be obtained crystalline and of a metallic lustre, by employing crystallized tungstic acid, such as is obtained by decomposing *tungstate of ammonia* in close vessels. The oxide in this state has, when pressed together, a deep copper colour. By pouring dilute hydrochloric acid on tungstic acid, and placing in the liquor a strip of *zinc*, it is gradually decomposed, and oxide of tungsten is obtained in the form of brilliant copper-coloured spangles, but it cannot be preserved or even dried in this state. It may also be obtained in the form of a beautiful violet-brown precipitate, by mixing *chloride of tungsten* with water, but it is very unstable: the oxide obtained in the dry way may be preserved without alteration. When heated below redness, it burns like tinder, and is converted into tungstic acid. It does not appear to form salts with acids, but it dissolves in concentrated *caustic potassa* with the disengagement of heat and the formation of *tungstate of potassa.* This oxide is remarkable for a beautiful compound which it forms with *soda;* it is prepared by saturating fused *tungstate of soda* with tungstic acid, and reducing the mass by heat in a current of hydrogen gas: after having dissolved out the neutral undecomposed tungstate, the new compound remains in the form of regular cubes and scales of a golden-yellow colour, possessing metallic lustre, and having all the appearance of *gold.* It is not acted upon by any acid but the *hydrofluoric; aqua regia* has no action on it, but it is decomposed by *oxygen gas, sulphur,* and *chlorine,* at a high temperature. No such compound can be formed with *potassa* or with the alkaline earths.

Tungstic Acid (WO_3).—*General characters:* This acid is generally prepared by fusing a mixture of finely powdered *wolfram* with an equal weight of carbonate of potassa, and half its weight of nitre. The alkaline tungstate thus formed is dissolved in water exactly neutralized by nitric acid, precipitated by nitrate of mercury, and the precipitate calcined in a platinum crucible. It is of a fine yellow colour, becoming dark-

green when strongly heated; it also assumes a green tint by mere exposure to the rays of the sun; it is insoluble in water, but readily soluble in caustic alkalies. Hydrated tungstic acid is formed slowly as a gelatinous mass, by heating a diluted solution of an alkaline tungstate with dilute nitric acid; when washed and dried, it is a powder of a brilliant opaque yellow-grey colour. *Tungstic acid*, like *molybdic acid*, unites with other acids, acting the part of a base.

Zinc produces, in acid solutions of tungstic acid a beautiful blue colour, owing to the formation of *oxide of tungsten*.

Sulphide of tungsten is precipitated when a tungstate is decomposed by acids in the presence of *sulphide of ammonium*.

Before the blowpipe, tungstic acid is thus detected:—Mix a small portion of the mineral with five times its volume of *soda*, and heat strongly in a platinum spoon; dissolve in water, and precipitate the filtered solution with hydrochloric acid; the precipitate assumes, when heated, a beautiful *yellow* colour. The oxides of tungsten, when perfectly pure, liquefy with microcosmic salt in the oxidating flame; in the reducing flame they become *green*, and when cold beautiful *blue*. The glass, when treated with tin on charcoal in the reducing flame, assumes a darker colour, which on cooling is *green*.

77. Oxides of Vanadium. (VO; VO_2; VO_3.)

General characters.—Oxide of vanadium, obtained by reducing *vanadic acid* at a red-heat by a current of hydrogen gas, is a black crystalline powder; it is remarkable as being an excellent conductor of electricity, and as excelling, as a negative electromotive element, copper, and even gold or platinum. It has not hitherto been made to combine with either acids or bases. It oxidizes gradually in the air, and under water it acquires a fine green colour. Heated in the air, it takes fire and burns, leaving a black mass; by chlorine it is converted into *chloride* and *vanadic acid*.

78. Binoxide of Vanadium, or Vanadious Acid. (VO_2.)

The anhydrous oxide is a black powder which has no action on test paper. It is insoluble in water, but when left for some time in contact with that fluid it oxidizes, becoming by degrees green. The hydrate, which when first formed is greyish-white, oxidizes rapidly in the air, becoming first brown, then green, and finally black. The calcined oxide is slowly but completely

dissolved in acids; the solution is blue; though acting the part of a base, it nevertheless combines with bases, giving rise to a class of salts called *vanadites*. It is dissolved by alkaline carbonates; the solution, which is of a deep-brown colour, contains a *vanadite* and a *bicarbonate*. The bicarbonates also dissolve it, forming blue solutions, probably neutral double carbonates of the oxide and alkali.

79. Vanadic Acid. (VO_3.)

Prepared by decomposing *vanadate of ammonia* by heat. It is a rusty red-brown powder, without taste or smell. It supports a high temperature without losing oxygen; but at a red-heat it enters into fusion. In contact with organic matter at a red-heat, it loses oxygen. It strongly reddens litmus-paper. The fused acid crystallizes, on cooling, in the form of interlaced needles of a yellowish-red colour; but if a small quantity of oxide be present, it has a violet tint. It does not conduct electricity. It dissolves sparingly in water, forming a clear-yellow solution. It cannot be obtained crystalline in the humid way, nor can it be obtained pure out of solution, as it combines with acids as well as with bases. It is easily reduced to the state of oxide under the influence of an acid, such as *coloured nitric acid*, *sulphurous*, *oxalic*, or *tartaric acids*; *alcohol* and *sugar* likewise effect its reduction, blue oxide of vanadium being formed. Hydrochloric acid dissolves it, forming an orange-coloured solution; but after a while *chlorine* is disengaged, and the liquid acquires the property of dissolving gold and platinum.

Comportment of solutions of Binoxide of Vanadium with reagents.

Potassa produces a greyish-white hydrate, soluble in excess of *potassa*, but insoluble in *ammonia*.

Hydrosulphuric acid occasions no precipitate; but *sulphide of ammonium* produces a brownish-black precipitate, soluble in excess, the solution having a purple colour.

Comportment of solution of Vanadic Acid with reagents.

Nitrate of silver produces a yellow precipitate, becoming white by exposure to the air, and soluble in *nitric acid* and in *ammonia*.

Chloride of barium produces a bulky orange-yellow precipitate, slightly soluble in water.

Sulphide of ammonium gives a brown precipitate (VaS_3), soluble in excess, forming a brown liquid.

Ferrocyanide of potassium produces a fine green precipitate.

Chloride of ammonium produces a white flocculent precipitate of *vanadate of ammonia*, quite insoluble in hydrochloric acid.

Before the blowpipe, oxides of vanadium, heated in the outer flame with borax or microcosmic salt, give a yellow bead; in the inner flame a fine green one, which again becomes yellow in the outer flame. *Vanadic acid*, heated on charcoal, leaves a compact mass, the colour of plumbago (oxide of vanadium); with borax and microcosmic salt it gives a beautiful green glass, which while hot is brown. It is not coloured blue by the addition of tin. *Chromic acid* gives with borax and microcosmic salt a green bead; but *vanadic acid* is distinguished from *chromic acid* from the circumstance that the green bead in the former can be changed in the oxidating flame to yellow, which is not the case with the latter.

80. Oxides of Molybdenum. (MoO; MoO_2; MoO_3.)

General characters.—When to a solution of a *molybdate* in water, hydrochloric acid is added, and the mixture digested with *distilled zinc*, the latter becomes oxidized at the expense of the molybdic acid; and the liquid becomes first blue, then red, brown, and finally black. From this solution *potassa* precipitates *hydrated oxide of molybdenum* in the form of a black flocculent mass. This hydrate is dissolved with difficulty in acids; the solutions are opaque and almost black, unless greatly diluted; the taste is astringent, but not metallic. When heated to redness *in vacuo*, it takes fire, burning with vivid scintillations, and a hydrous oxide remains of a pitchy blackness, and insoluble in acids. Heated in the air, it burns, and is converted into *molybdic oxide* (MoO_2). *Oxide of molybdenum* is not soluble either in *caustic potassa* or in solutions of the *fixed alkaline carbonates*. It dissolves, however, in *carbonate of ammonia*.

81. Molybdic Oxide. (MO_2.)

When pure, it is a powder of a deep-brown colour; by the light of the sun it is *brilliant purple*. It is insoluble in alkalies and in acids, but it dissolves in small quantities in a mixture of *concentrated sulphuric acid* and *tartrate of potassa*. Nitric acid converts it into *molybdic acid*. Hydrated molybdic oxide is similar in appearance to *hydrated sesquioxide of iron*. It is,

to a certain extent, soluble in water, the solution having a deep-red colour, and it appears to form, with some acids, subsalts, which are soluble. If dried by exposure to the air, it acquires a blue colour on the surface from the absorption of oxygen; the solution in water reddens litmus-paper; it has an astringent and somewhat metallic taste. It is completely precipitated by sal-ammoniac, and when once dried cannot again be dissolved in water. Heated *in vacuo*, it loses its water, and brown anhydrous oxide remains. Though it reddens litmus-paper, it has none of the other properties of an acid. Caustic alkalies do not dissolve it, though it is soluble in alkaline carbonates. The solution in *carbonate of ammonia* is entirely precipitated by boiling, and that in *carbonate of potassa* is by degrees converted into *molybdate of potassa.*

82. Molybdic Acid. (MO_3.)

When pure, it is a light, porous, white mass; and when diffused through water it assumes the appearance of extremely small, silky, brilliant, crystalline scales. Heated to redness, it melts into a deep-yellow liquid, which, on cooling, becomes pale straw-yellow and crystalline, and on breaking, divides into crystalline spangles. In close vessels it supports a strong red-heat without volatilizing; but in open vessels it sublimes at its fusing-point, its surface becoming covered with crystalline spangles. Water dissolves it in small quantities (about $\frac{1}{570}$ of its weight). The solution has a feeble metallic taste, and reddens litmus-paper. Before calcination it is soluble in acids, forming compounds in which it acts the part of a base. It dissolves also in a saturated solution of *tartrate of potassa*, and in solutions of *caustic* and *carbonated alkalies.*

Comportment of solutions of Oxide of Molybdenum with reagents.

Potassa and *ammonia* produce a brownish-black precipitate, insoluble in excess of the precipitants.

Carbonate of potassa and *carbonate of ammonia* produce a similar precipitate, slightly soluble in *carbonate of potassa*, more soluble in *carbonate of ammonia.*

Sulphide of ammonium gives a yellowish-brown precipitate, soluble in excess of the precipitant.

Molybdic oxide is distinguished from *oxide of molybdenum* by its greater solubility in *carbonate of potassa.*

Behaviour of Molybdic Acid with reagents.

Nitrate of silver produces a white precipitate, soluble in much water and in *nitric acid* and in *ammonia*.

Chloride of barium produces a similar precipitate, soluble in *nitric acid*.

Hydrosulphuric acid, added in excess to an acid solution, produces, after a time, a brown precipitate, subsiding slowly; the supernatant fluid being blue or green.

Metallic zinc or *tin* produces, in solutions containing free hydrochloric acid, a blue colour, which becomes green and finally black.

Before the blowpipe, the oxides of molybdenum give to microcosmic salt in the inner flame a fine *green* colour, becoming more perceptible on cooling; with borax they produce in the inner flame a *brownish-red* bead.

General Remarks on the Oxides of the Fifth Group, Section B.

Of the metallic oxides comprehended in this section, it will only be necessary to make a few remarks on the method of detecting *tin*, *antimony*, and *arsenic* when these metals exist together in a compound. The three metals are obtained in the form of sulphides (SnS_2; SbS_5; AsS_5) by precipitating their solution in sulphide of ammonium by an acid. Having washed the precipitate, it may be agitated for some time with a slightly warmed solution of *sesquicarbonate of ammonia:* thrown on a filter, and washed with sesquicarbonate of ammonia as long as the washings give a distinct yellow precipitate on the addition of hydrochloric acid, the whole of the arsenic will be found in the alkaline solution; but as some *bisulphide of tin* may likewise have been dissolved, it is necessary to reprecipitate by the addition of hydrochloric acid, and having washed the precipitate, to redissolve it in warm ammonia; the ammoniacal solution should be evaporated to dryness, and the residue tested specially for arsenic. The greater part of the *bisulphide of tin*, and the whole of the *pentasulphide of antimony* will have remained undissolved by the sesquicarbonate of ammonia: it should be boiled with aqua-regia, and then mixed with excess of sesquicarbonate of ammonia; this precipitates *binoxide of tin* (which must be specially tested), the antimony remaining in the alkaline solution, from which it is precipitated of its characteristic orange-colour, by mixing with slight excess of hydrochloric acid, and then saturating with sulphuretted hydrogen.

CHAPTER IV.

ON THE COMPORTMENT OF THE PRINCIPAL INORGANIC AND ORGANIC ACIDS WITH REAGENTS.

83. ALTHOUGH the acids cannot be classified with the same degree of perspicuity with which we are enabled to arrange the bases, there are certain reagents by which we may, for analytical purposes, divide them conveniently into groups, the subdivision of which may afterwards be effected by other reagents, which are called *special*.

The reagents for grouping the *inorganic acids* are *chloride of barium* and *nitrate of silver;* those for grouping the *organic acids* are *chloride of calcium* and *sesquichloride of iron.*

A.—Inorganic Acids.

I.—*Acids precipitated by chloride of barium.*

Carbonic, sulphurous, hyposulphurous, hyposulphuric, sulphuric, selenic, phosphoric, phosphorous, hypophosphorous, boracic, silicic, hydrofluoric, chromic, arsenic; arsenious, and other metallic acids.

II.—*Acids precipitated by nitrate of silver.*

Hydrochloric, hydrobromic, bromic, hydriodic, iodic, periodic, hydrocyanic, hydrosulphocyanic, hydroferrocyanic, hydroferridcyanic, hydrosulphuric acids.

III.—*Acids precipitated by neither chloride of barium nor nitrate of silver.*

Nitric, nitrous, perchloric, chloric, and chlorous acids.

B.—Organic Acids.

I.—*Acids precipitated by chloride of calcium.*

Oxalic, tartaric, pyrotartaric, citric, and malic acids.

II.—*Acids precipitated by sesquichloride of iron.*
Succinic, benzoic, tannic, and gallic acids.

III.—*Acids precipitated by neither chloride of calcium nor sesquichloride of iron.*
Acetic, formic, uric, and meconic acids.

A.—INORGANIC ACIDS.

I.—Acids precipitated by Chloride of Barium.

84. Carbonic Acid. (CO_2.)

General characters.—At common temperatures and pressures, this acid is a colourless, transparent, irrespirable, and incombustible gas. It is heavier than atmospheric air in the proportion of 1·5 to 1, and totally unfit for supporting combustion. It has a faintly sour and somewhat astringent taste. It reddens litmus-paper, but as the gas volatilizes the blue colour returns. It may be poured from one vessel to another, and a small animal exposed to its influence instantly dies in strong convulsions. It is decomposed at a red-heat in contact with carbon and other combustibles, carbonic oxide, an inflammable gas, being produced. A succession of electric sparks likewise decomposes it into carbonic oxide and oxygen. Water at ordinary temperatures and pressures absorbs rather more than its own volume of carbonic acid gas, and considerably more at a low temperature and under pressure. The solution has an agreeable, piquant, and feebly acid taste. At a temperature of 0°, and under a pressure of 36 atmospheres, it is condensed into a colourless liquid, and by peculiar management it may even be obtained in the solid state, having the appearance of a mass of snow. All the neutral carbonates, with the exception of those of the alkalies, are *insoluble* or very sparingly soluble in water; they are, however, decomposed by nearly all acids that are soluble in water, the carbonic acid gas escaping with effervescence; but, to expel the whole, excess of acid must be added, in consequence of the formation of *bicarbonates*. Most of the carbonates lose their acid by ignition.

Comportment of the soluble Carbonates with reagents.

(Solution of Carbonate of Soda may be used.)

Lime water and *baryta water* produce white precipitates, in-

soluble in water, but soluble with effervescence in hydrochloric acid.

$$(1.)\ NaO,CO_2 + BaO,HO = BaO,CO_2 + NaO + HO.$$

$$(2.)\ BaO,CO_2 + HCl = BaCl + HO + CO_2.$$

Chloride of barium and *chloride of calcium* produce white precipitates in solutions of neutral alkaline carbonates; but in solutions of *bicarbonates* no precipitate is formed until the second atom of carbonic acid is expelled by boiling, because both *bicarbonate of baryta* and *bicarbonate of lime* are soluble in water.

Nitrate of silver produces a white precipitate of carbonate of silver soluble with effervescence in *nitric* acid.

Characteristic.—The solid carbonates (also their solutions, if not too dilute) are all decomposed by *hydrochloric* and *nitric* acid; and by most other acids, with effervescence. The gas evolved is recognized as carbonic acid by producing a white turbidity when passed into *baryta water*, *lime water*, or *solution of basic acetate of lead.*

85. Sulphurous Acid. (SO_2.)

General characters.—At common temperatures and pressures it is a permanent gas, of a suffocating odour and a very disagreeable taste, not inflammable nor possessing the power of supporting combustion. It is very fatal to animal life. It is absorbed in large quantities by water, and still more copiously by alcohol. It destroys the colour of vegetable substances. Its acid properties are very weak. All acids but *carbonic* and *hydrocyanic acids* displace it from its combinations. The class of salts which it forms are called *sulphites;* they are all insoluble, or very sparingly soluble, in water, but those of the alkalies. All the acid salts of sulphurous acid are soluble. At a low temperature and under pressure, it is reduced to a liquid.

Comportment of solutions of Sulphites with reagents.

(Solution of Sulphite of Ammonia may be used.)

Chloride of barium and *chloride of calcium* produce a white precipitate, soluble in hydrochloric acid; if, however, the solution of the sulphite has been for some time exposed to the air, this precipitate is no longer completely soluble in hydrochloric acid.

Protonitrate of lead produces a white precipitate, soluble in cold nitric acid, but decomposed when boiled, *sulphate of lead* being precipitated, and nitrous fumes evolved.

Nitrate of silver produces a white precipitate (AgO,SO_2), becoming black by the application of heat, the metal being reduced, and sulphuric acid formed. Thus :—

$$AgO,SO_2=Ag+SO_3.$$

Protochloride of tin, acidified with hydrochloric acid, produces a yellowish-brown precipitate.

$$2(NaO,SO_2)+6SnCl+2HCl=$$
$$SnS_2+2NaCl+2SnO_2+3SnCl_2+2HO.$$

Chloride of barium, when *boiled* with a solution of a sulphite, together with nitric acid, produces a white precipitate (BaO,SO_3).

Chlorine, nitric acid, and *fused nitre* convert *sulphites* into *sulphates*.

Solid sulphites, when moistened with an acid, evolve sulphurous acid, which may be recognized by its odour; when ignited in a glass tube, they are decomposed into *sulphides* and *sulphates*, and on treating the fused mass with a diluted acid, *hydrosulphuric acid* gas is disengaged, provided the metallic sulphide belongs to that class which decomposes water with the assistance of an acid.

Sulphuretted-hydrogen water produces in solutions containing sulphurous acid a white precipitate of *sulphur*.

Zinc in the presence of free hydrochloric acid evolves from solutions of sulphites, sulphuretted hydrogen.

Characteristic.—Its odour, and the formation of blue *iodide of starch* when a glass rod, moistened with starch paste, is introduced into the gas. Sulphurous acid is completely absorbed by *peroxide of lead*.

$$PbO_2+SO_2=PbO,SO_3.$$

86. HYPOSULPHUROUS ACID (DITHIONOUS ACID). (S_2O_2.)

The aqueous solution of this acid decomposes spontaneously into *sulphurous* acid and sulphur; the compounds which it forms with alkalies and alkaline earths are, with the exception of hyposulphite of baryta, soluble in water.

Comportment of solutions of Hyposulphites with reagents.

(Hyposulphite of Soda may be used.)

Chloride of barium in concentrated solutions occasions a white precipitate.

Nitrate of silver produces a precipitate which at first is

white, but it rapidly becomes yellow, and finally black; *sulphide of silver* being formed and nitric acid set free. Thus:—

$$AgO,NO_5 + NaO,S_2O_2 = AgS + NaO,SO_3 + NO_5.$$

Hydrochloric acid produces a yellow precipitate of sulphur, sulphurous acid being set free. Thus:—

$$NaO,S_2O_2 + HCl = NaCl + SO_2 + HO + S.$$

Characteristic.—Solutions of soluble hyposulphites possess the property of dissolving recently precipitated *chloride of silver;* the solution has an intensely sweet taste, leaving one of that nauseous bitterness peculiar to salts of silver. With *iodine,* solutions of hyposulphites produce an *iodide* and a *tetrathionate.* Thus:—

$$2(BaO,S_2O_2) + I = BaI + BaO,S_4O_5.$$

This reaction serves to distinguish between *sulphurous* and *hyposulphurous acids.*

87. Hyposulphuric Acid (Dithionic Acid). (S_2O_5.)

The aqueous solution of this acid, when heated, is resolved into *sulphuric* and *sulphurous acids;* its salts undergo the same decomposition by hydrochloric acid, aided by heat. Thus:—

$$NaO,S_2O_5 = NaO,SO_3 + SO_2.$$

The hyposulphates are generally soluble in water.

88. Sulphuric Acid. (SO_3.)

General characters.—In its pure anhydrous state it forms a tenacious crystalline mass resembling *asbestos;* exposed to the air, it gives off thick opaque fumes; its affinity for water is so powerful, that it hisses like a red-hot iron when brought into contact with it. By distilling crystallized protosulphate of iron, a *hydrated* acid is obtained which fumes when exposed to the air (*Nordhausen acid,* $2SO_3,HO$). *Monohydrate* of sulphuric acid (HO,SO_3) does not fume, but has an oily consistence; hence its commercial name, *oil of vitriol.* When pure it is colourless, the dark tinge that the acid sometimes has, arising from the separation of carbon from organic substances, which it rapidly decomposes. It has a powerful affinity for water, abstracting it from the atmosphere with great rapidity; during its combination with water great heat is evolved; the monohydrated acid freezes at 31°, and boils at 617°; it distils without alteration; its acid properties are exceedingly powerful; it displaces all other acids from bases at temperatures below its boiling-point; but at a higher temperature it is itself displaced

by certain weaker acids which are not volatile; the greater number of its compounds with bases are soluble in water; the sulphates of *baryta*, *strontia*, and *lead* are, however, nearly insoluble, the first entirely so.

Comportment of solutions of Sulphates with reagents.
(Solution of Sulphate of Soda may be used.)

Chloride of barium produces an immediate white precipitate (BaO,SO_3), even in highly dilute solutions, insoluble in water, but not altogether insoluble in dilute hydrochloric and nitric acids. The solution to be precipitated should not contain too much *nitric* or *hydrochloric acid*, as baryta salts which are very *soluble* in water are very sparingly so in acids; and a white precipitate might be formed which could be mistaken for *sulphate of baryta*. Such a precipitate would, however, be readily soluble in water.

Acetate of lead produces a white precipitate, soluble to a slight extent in dilute nitric acid, but completely insoluble in *boiling and concentrated* hydrochloric acid.

The sulphates of the alkaline earths and alkalies are not decomposed by heat alone; when heated in contact with charcoal, they are reduced to *sulphides:* the reduction is facilitated by mixture with carbonate of soda. On treating the reduced mass with an acid, *sulphuretted hydrogen* is evolved, which may be detected by the odour, by lead paper, or by making the experiment on a bright silver surface. All the other sulphates, with the exception of that of *oxide of lead*, are decomposed at a high temperature, *sulphuric acid*, or a mixture of *sulphurous acid* and *oxygen*, being set free, and pure oxides, or the metals themselves left. Insoluble sulphates are converted into carbonates by fusion with carbonate of soda, alkaline sulphates being formed.

Before the blowpipe, colourless sulphates may be detected by fusing them with *silicate of soda* in the reducing flame; a sulphide is thereby formed, and the glass assumes a red or dark-yellow colour, according to the quantity of acid present. *Coloured* sulphates are detected by fusing them with two parts of soda and one of borax, in the reducing flame, on charcoal, and placing the fused mass on a plate of silver, and moistening it with water. A tarnishing of the metal indicates *sulphur*.

Characteristic reaction.—That with *chloride of barium*.

89. Selenic Acid. (HO,SeO_3.)

This acid produces a precipitate with *chloride of barium*, which is insoluble in nitric acid. *Seleniate of baryta* is, however, decomposed by boiling hydrochloric acid, chlorine being evolved. This is not the case with *sulphate of baryta*.

90. Phosphoric Acid. (PO_5.)

General characters.—When anhydrous, it has the form of white flakes, which rapidly absorb moisture from the atmosphere, becoming a syrupy liquid which has a free acid, but not caustic taste; if pure, it volatilizes without residue when strongly heated in an open platinum vessel; it attacks vessels of glass or porcelain when fused therein. The alkaline phosphates are soluble in water, but the neutral compounds of phosphoric acid with the earths and metallic oxides are insoluble in water, though they dissolve in excess of phosphoric acid and in nitric acid.

Phosphoric acid forms with water three distinct hydrates: HO,PO_5, *metaphosphoric acid;* $2HO,PO_5$, *pyrophosphoric acid;* $3HO,PO_5$, *ordinary phosphoric acid*, besides modifications.

Comportment of solutions of Metaphosphates with reagents.

Nitrate of silver produces a white gelatinous precipitate (AgO,PO_5), soluble in excess of metaphosphate of soda.

Chloride of barium gives a voluminous white precipitate (BaO,PO_5).

Acetate of lead occasions a white precipitate (PbO,PO_5).

Metaphosphoric acid strongly coagulates the *albumen* of white of egg, by which character it is most distinctly recognized; a solution of an alkaline metaphosphate does not coagulate albumen, neither does *acetic acid;* but if the two be mixed, the albumen becomes coagulated in consequence of the liberation of metaphosphoric acid by the acetic acid. Metaphosphoric acid passes by boiling into ordinary phosphoric acid ($3HO,PO_5$): the conversion is accelerated by the addition of sulphuric acid.

Comportment of solutions of Pyrophosphates with reagents.

Neither *chloride of barium* nor *chloride of calcium* precipitate this acid in the free state.

Nitrate of silver produces in solutions of alkaline pyrophosphates a white flaky precipitate ($2AgO,PO_5$).

Acetate of lead gives a white precipitate ($2PO,PO_5$). Neither

pyrophosphoric acid nor any of its soluble salts have the property of precipitating albumen.

Pyrophosphoric acid and solutions of pyrophosphates are converted into ordinary phosphoric acid and phosphates, by boiling with the mineral acids.

Comportment of solutions of Tribasic or ordinary Phosphates, with reagents.

(Solution of Rhombic or common Phosphate of Soda may be used.)

Chloride of barium produces a white precipitate, soluble in hydrochloric acid.

Chloride of calcium occasions a white precipitate, soluble in hydrochloric and acetic acids, and re-precipitated by ammonia.

Nitrate of silver produces a *lemon-yellow* precipitate ($3\,AgO, PO_5$) soluble in nitric acid and in ammonia.

Acetate of lead gives a white precipitate ($3\,PbO, PO_5$), soluble in nitric acid, but insoluble in ammonia, and in acetic acid. This precipitate, when fused on charcoal in the outer blowpipe flame, forms a bead which crystallizes on cooling.

Sesquichloride of iron produces in neutral, or slightly alkaline solutions, a *yellowish-white* precipitate ($Fe_2O_3 PO_5$), which is soluble in hydrochloric acid, but quite insoluble in *acetic acid.* If the hydrochloric solution of any mineral containing phosphoric acid be nearly neutralized by ammonia or carbonate of soda, excess of acetate of soda or acetate of potash added, and then sesquichloride of iron in small excess, a reddish-brown precipitate will be obtained on boiling the mixture, which will contain the whole of the phosphoric acid. This precipitate should be thrown on a filter and well washed with boiling water, after which it is to be dissolved in dilute hydrochloric acid, avoiding great excess, and digested with *ammonia* and *sulphide of ammonium;* it is hereby decomposed into *sulphide of iron* (insoluble) and *phosphate of ammonia* (soluble), the black mass is thrown on a filter, the filtrate concentrated by evaporation, filtered again (if necessary), and the filtrate treated in accordance with the following.

Sulphate of magnesia and *other soluble magnesian salts* produce in solutions of phosphates of the alkalies a crystalline precipitate, which makes its appearance only gradually; but if *ammonia* be added, a crystalline precipitate of *phosphate of magnesia and ammonia* ($2\,MgO, NH_4O, PO_5$) immediately subsides, and is favoured by agitation. This precipitate is insoluble

in ammonia and in ammoniacal salts, but is soluble in free acids. Previous to the application of this test, *chloride of ammonium* should be added to the solution in considerable quantity in order to prevent the precipitation of hydrate of magnesia.

Acetate of sesquioxide of uranium precipitates phosphoric acid as *yellow double phosphate of sesquioxide of uranium and ammonia.* If the compound to be tested be an earthy phosphate, it should be dissolved in hydrochloric acid, concentrated by evaporation, ammonia added in very slight excess, then acetic acid and acetate of ammonia, and finally heated to boiling with acetate of sesquioxide of uranium, upon which the yellow precipitate makes its appearance.

Molybdate of ammonia produces in solutions containing phosphoric acid a yellow precipitate. To the solution, after the addition of the molybdate, nitric acid should be added, it should then be warmed, it will speedily assume a yellow colour, and a yellow precipitate will gradually subside. This test is especially useful, as it enables the operator to detect the presence of phosphoric acid in minute quantities, in acid solutions of soils, fossils, etc.

Characters of the different forms of the Tribasic Alkaline Phosphates.

When a salt of tribasic phosphoric acid, with three atoms of a fixed base which is strongly *alkaline*, is mixed with neutral nitrate of silver, a yellow precipitate is formed, and the solution is perfectly neutral to test-paper.

$$3NaO,PO_5 + 3(AgO,NO_5) = 3AgO,PO_5 + 3(NaO,NO_5).$$

Salts of tribasic phosphoric acid with two atoms of fixed base have also an *alkaline* reaction. They give with neutral nitrate of silver the same yellow precipitate, and the mixture is *acid* to test-paper.

$$2NaO,HO,PO_5 + 3(AgO,NO_5) =$$
$$3AgO,PO_5 + 2(NaO,NO_5) + HO,NO_5.$$

When these latter salts are ignited, they are converted into *pyrophosphates* (bibasic), which when dissolved in water exhibit an alkaline reaction, and give with neutral nitrate of silver a *white* precipitate; after the precipitation, the solution is *neutral.*

$$2NaO,PO_5 + 2(AgO,NO_5) = 2AgO,PO_5 + 2(NaO,NO_5).$$

Salts of tribasic phosphoric acid with one atom of fixed

base have a strong *acid* reaction; they give with neutral nitrate of silver a yellow precipitate, the solution being acid to test-paper.

$$NaO,2HO,PO_5 + 3(AgO,NO_5) =$$
$$3AgO,PO_5 + NaO,NO_5 + 2(HO,NO_5).$$

When ignited, these latter salts pass into *metaphosphates* (monobasic). The metaphosphate of potash is very sparingly soluble in water, but the metaphosphate of soda dissolves readily, and the solution gives with nitrate of silver a white precipitate soluble in excess of the precipitant.

Before the blowpipe, phosphoric acid is detected by the following method of Berzelius:—Dissolve the subject of examination in boracic acid, upon charcoal, in the oxidating flame; introduce into the melted bead a piece of fine iron-wire, and expose the whole to a strong reducing-flame. The iron oxidizes at the expense of the phosphoric acid, and *borate* and *phosphate of iron* are produced. The latter fuses in a strong red heat. When cold, the glass is removed from the charcoal, and broken into pieces on an anvil, between folds of paper. A globular metallic button of *magnetic phosphide of iron* is thus produced. This operation requires skill on the part of the operator. To detect phosphoric acid in an aluminous compound, Berzelius gives the following method:—The substance, pulverized in an agate mortar, is rubbed with a mixture of six parts of soda, and one and a half of silica, and the mass fused on charcoal in the oxidating flame. The fused residuum is boiled with water, in which phosphate and the excess of carbonate of soda dissolve, leaving the alumina in combination with silicic acid. The phosphoric acid is detected in aqueous solution as above directed.

Characteristic reactions.—Those with *nitrate of silver*; with *sulphate of magnesia* in the presence of *ammonia*; and with *molybdate of ammonia*.

91. Phosphorous Acid. (PO_3.)

General characters.—In its anhydrous state, it is a white, but not a crystalline powder. Its hydrate may be obtained in the form of deliquescent crystals, by evaporating the aqueous solution obtained by acting on *sesquichloride of phosphorus* by water. It slowly absorbs oxygen from the air, becoming converted into phosphoric acid. By boiling and fusion it is decomposed, phosphuretted hydrogen being formed, which in-

flames on the approach of a burning body, fumes of phosphoric acid making their appearance.

$$4PO_3 + 3HO = PH_3 + 3PO_5.$$

The alkaline *phosphites* are soluble in water, and are powerful deoxidizing agents. They reduce solutions of *gold* and *silver*, and salts of *copper* and *mercury*; passing into *phosphates*. *Sulphurous acid* when warmed with *phosphorous acid* yields a precipitate of sulphur, and when an excess of the latter is used, *hydrosulphuric acid*.

$$3PO_3 + 2SO_2 + 2HO = 3PO_5 + 2HS\text{; and}$$
$$SO_2 + 2HS = 2HO + S_3.$$

Heat also converts them into *phosphates*, hydrogen gas being evolved, which burns with a blue flame without producing any fumes of phosphoric acid. *Hypophosphites* are distinguished from *phosphites* from their giving rise to a spontaneously inflammable phosphuretted hydrogen when strongly heated, fumes of phosphoric acid being formed. All the *hypophosphites* are soluble in water.

92. Boracic Acid. (BO_3.)

General characters.—This acid crystallizes, out of its aqueous solution, in brilliant scales, which are greasy to the touch. It has no smell, and a very faint acid taste. It is sparingly soluble in water. In the presence of aqueous vapours it sublimes easily, but alone it is perfectly fixed at a red-heat, at which, however, it fuses into a colourless, transparent, brittle glass. It dissolves in alcohol, to the flame of which it communicates a green tinge, a property which is characteristic of this acid. It volatilizes with the vapour of alcohol, as with that of water. The alkaline borates are soluble in water, but the borates of the earths and metallic oxides are almost insoluble, though they dissolve readily in acids and ammoniacal salts. They are all very fusible, and promote the fusion of other bodies when mixed with them; hence their uses as fluxes. Free boracic acid reddens turmeric-paper like an alkali.

Comportment of solutions of Borates with reagents.

(Solution of Biborate of Soda (Borax) ($NaO,2BO_3$) may be used.)

Chloride of barium produces a white precipitate (BaO,BO_3), soluble in acids and in ammoniacal salts, and in a large quantity of water.

Nitrate of silver, in concentrated solutions, produces a white precipitate, soluble in ammonia and in dilute nitric acid.

Chloride of calcium produces a white precipitate, soluble in acids and in ammonia, and in a large quantity of water.

Acetate of lead produces a white precipitate, soluble in acids.

Nitrate of suboxide of mercury produces an olive-brown precipitate, soluble in nitric acid and in ammonia.

Hydrochloric and *sulphuric acids* separate *boracic* acid from solutions of borates, at a boiling temperature, in the form of crystalline scales.

Biborate of soda ($NaO,2BO_3$) precipitates solution of *sesquichloride of iron*. The precipitate dissolves on heating to a dark-red liquid, which might be mistaken for the reaction produced between *acetic acid* and the same reagent; if the solutions are not very concentrated, only a darker colour is observable, and no precipitate.

Before the blowpipe, the following method of detecting boracic acid in salts and minerals has been recommended by Turner:—Knead into a paste, with a few drops of water, a mixture of the finely divided substance, with 4½ parts of *bisulphate of potassa*, and 1 of powdered *fluor-spar*, and fuse the mass on the ring of the platinum wire. At the apex of the blue flame *fluoboric acid* gas is liberated, which communicates to the outer flame a pure-green colour.

Characteristic.—If a pulverized borate be moistened in a porcelain capsule with a few drops of sulphuric acid, and covered with alcohol, warmed and inflamed, the flame will have a green tinge, most perceptible at its borders. The presence of *chlorides* interferes with this test, in some measure, in consequence of the formation of hydrochloric ether; the flame, however, in this case, has a decided *blue* tinge.

93. Silicic Acid. (SiO_2)

General characters.—Of this acid there are two isomeric modifications; one is insoluble in water, and resists the action of all acids but *hydrofluoric*. It is a white, tasteless powder, gritty between the teeth, and infusible at the strongest heat of a furnace, but fusing before a blowpipe flame urged with oxygen, into a limpid, colourless liquid. This form of silicic acid exists nearly in a state of purity in *rock crystal* and in *white quartz*. By fusion with carbonate of potassa, or with a mixture of carbonate of potassa and carbonate of soda, all siliceous minerals are decomposed, basic alkaline silicates being formed, which are soluble in water, and from which

acids separate silicic acid in its soluble modification; but, by drying, it again returns to the insoluble state. The soluble variety of silicic acid is obtained in the form of a gelatinous mass, by passing the gas obtained by heating together a mixture of powdered fluor-spar and quartz, with sulphuric acid, into water. In this state water dissolves a small quantity, without, however, acquiring any taste, or the property of reddening litmus-paper. By evaporation, the acid is obtained as a white, earthy, but not crystalline mass, which may again be dissolved in water; but, if a strong mineral acid be added to the water during its evaporation, the dry silicic acid is no longer soluble in water. Gelatinous silicic acid is soluble, to a considerable extent, in acids. No precipitation is, therefore, observed on adding hydrochloric acid to a dilute solution of an alkaline silicate, until the liquid has been concentrated by evaporation. In most siliceous minerals, silicic acid exists in its insoluble form. There are, however, a number of native hydrated silicates, denominated *zeolites*, which contain silicic acid in its soluble form, and which are, therefore, decomposed by concentrated hydrochloric acid even in the cold, forming a gelatinous mass soluble in water. There are other minerals which are only dissolved in hydrochloric acid by prolonged digestion, the silicic acid separating as a flaky powder, and not as a jelly. At ordinary temperatures, silicic acid is one of the weakest of the acids, dissolving in a boiling solution of the fixed alkaline carbonates, without expelling their carbonic acid; but at high temperatures it is capable of expelling all the volatile acids, not even excepting the sulphuric acid, from their combinations.

Diluted solutions of alkaline silicates, when nearly neutralized by nitric acid, are precipitated by most heavy oxides, and by the salts of the *alkaline earths* and by *ammonia*. The first step, therefore, in analysing a mineral containing silicic acid, is to convert the silicic acid from its soluble to its insoluble condition, which is done by evaporating the hydrochloric solution to perfect dryness, and then dissolving out with acid the basic metallic oxides.

Before the blowpipe, silicic acid is recognized by means of microcosmic salt and soda; the examination is generally performed on a platinum wire. The microcosmic salt is first fused into a bead, the silicate added, and the whole heated in the oxidizing flame; the glass bead, while hot, is clear, and the

separated silicic acid floats through it in a collected state; the bases combine with the free acid in the flux. Silicic acid with soda, on charcoal, gives a clear bead, carbonic acid escaping with effervescence; even when a small quantity of an earth is present, it still fuses to a clear glass. This is the case with *felspar;* but, if the silicate contain a large proportion of a non-alkaline base, the compound becomes infusible.

Silicic acid is separated from *titanic acid* by fusion with bisulphate of potassa in a platinum crucible; from the fused mass the titanic acid may be extracted by water.

94. Hydrofluosilicic Acid. (HF.)

General characters.—This acid is very volatile and corrosive, giving off dense fumes in the air; it is distinguished from all other acids by its property of dissolving the insoluble form of silicic acid; it cannot therefore be preserved in glass vessels. It combines with water with the same energy as sulphuric acid. It decomposes metallic oxides, giving rise to water and *metallic fluorides.* Towards metals it behaves in general in the same manner as the oxyacids, and it dissolves copper and silver gradually with the disengagement of hydrogen; in its concentrated state it acts on many substances with great energy, dissolving some bodies which are not acted on even by boiling aqua-regia, such as *silicic, titanic, molybdic,* and *tungstic acids.* The concentrated acid acts with extreme violence on the skin, causing painful ulcers very difficult to heal. The alkaline fluorides are soluble in water, as are also the fluorides of *aluminum, tin, iron,* and *mercury.* The fluorides of the metals of the alkaline earths are almost insoluble, as are also the fluorides of *copper, lead,* and *zinc,* though they dissolve more or less readily in hydrofluoric acid. The greater number of the fluorides bear ignition without being decomposed; the insoluble fluorides are decomposed by fusion with alkaline carbonates.

Comportment of solutions of Fluorides with reagents.

(Solution of Fluoride of Potassium (KF) may be used.)

Chloride of barium produces a white precipitate soluble in hydrochloric acid.

Chloride of calcium produces a gelatinous and very transparent precipitate, almost insoluble in free acids, even in hydrofluoric acid, and in alkalies in the cold; the addition of ammonia causes the complete subsidence of the precipitate (CaF).

Acetate of lead occasions a white precipitate soluble in hydrochloric acid.

Sulphuric acid at the boiling temperature decomposes all fluorides with the disengagement of hydrofluoric acid. The experiment is made by tracing lines on a plate of glass, covered with beeswax, with a wooden point, so as to expose the glass; and laying the plate on a platinum crucible containing the pulverized fluoride and concentrated sulphuric acid. A moderate heat insufficient to melt the wax, is applied to the crucible for a few minutes. The exposed lines are found etched, on the removal of the wax, which is effected by spirits of turpentine.

When a fluoride is mixed with a substance containing silicic acid, such as pounded glass, and heated together with concentrated sulphuric acid, fluosilicic acid is formed. Thus:—

$$SiO_2 + 2CaF + 2(HO,SO_3) = SiF_2 + 2(CaO,SO_3) + 2HO.$$

This acid is disengaged as a gas which fumes strongly in a moist atmosphere, and when brought into contact with water is decomposed, with the separation of silicic acid in its gelatinous form, and the formation of *hydrofluosilicic acid*. Thus:—

$$3SiF_2 + 2HO = 2(HF,SiF_2) + SiO_2.$$

This interesting reaction is observed by heating the materials in a test-tube, and conveying the gas, by a bent tube, into another test-tube containing water.

By cautiously fusing in a test-tube equal parts of a finely pulverized fluoride, and bisulphate of potassa, hydrofluoric acid is rendered evident by the roughening and loss of transparency of the upper part of the tube.

95. Chromic Acid. (CrO_3).

General characters.—This acid is obtained by the decomposition of bichromate of potassa by sulphuric acid, in the form of brilliant crimson needles, which absorb moisture from the air and pass into a deep-brown viscous fluid; evaporated to dryness it is, while hot, black, but on cooling it becomes deep-red; it has no smell; its taste is strongly acid, but not metallic; it tinges the skin yellow. It is soluble in alcohol; but the solution decomposes by the action of heat and light, an ether being formed, and hydrated oxide of chromium precipitated. When alcohol is dropped on the concentrated acid, it takes fire, and the acid becomes incandescent; an aqueous solution of chromic acid is gradually decomposed by the light of the sun, oxygen gas being liberated. All its salts are coloured yellow

or red; the alkaline chromates and bichromates are soluble in water; most of the other salts of chromic acid are insoluble in water, though they are all soluble in nitric acid.

Comportment of solutions of Chromates with reagents.

(Solution of Chromate of Potassa (KO,CrO_3) may be used.)

Chloride of barium produces a pale-yellow precipitate, soluble in nitric and hydrochloric acids.

Acetate of lead produces a yellow precipitate, soluble in potassa, and sparingly soluble in nitric acid.

Nitrate of silver produces a dark-purple precipitate soluble in nitric acid, and in ammonia.

Subnitrate of mercury produces a brick-red precipitate.

Hydrosulphuric acid in neutral solutions reduces the chromic acid with the precipitation of sulphur, and oxide of chromium. Thus:—

$$2(KO,CrO_3) + 5HS = 2KS + 5HO + Cr_2O_3 + S_3$$

In the presence of a free acid the oxide of chromium is dissolved, at least in part, and sulphur precipitated.

Sulphurous acid likewise reduces chromic acid, *sulphuric* and *hyposulphuric* acids being formed.

Oxalic, *tartaric*, and *citric acids*, reduce the acid to sesquioxide of chromium, carbonic acid being evolved.

Hydrochloric acid, and *alcohol*, or *zinc*, on being boiled with solution of a chromate, reduce the acid, the fluid becoming green.

Insoluble chromates are decomposed by fusion with alkaline carbonates, alkaline chromates being formed.

Solid chromates when heated with concentrated sulphuric acid evolve oxygen gas. Thus:—

$$(KO,2CrO_3) + 4SO_3 = KO,SO_3 + (Cr_2O_3,3SO_3) + O_3.$$

Solid chromates when heated with concentrated sulphuric acid and chloride of sodium disengage chlorochromic acid (CrO_2Cl).

$$NaCl + KO,CrO_3 + 4(HO,SO_3) =$$
$$NaO,SO_3,HO,SO_3 + KO,SO_3,HO,SO_3 + CrO_2Cl + 2HO.$$

Chlorochromic acid is decomposed by water into chromic and hydrochloric acids. Thus:—

$$CrO_2Cl + HO = CrO_3 + HCl$$

Characteristic reactions.—Those with *nitrate of silver* and *acetate of lead;* and with *hydrochloric acid* and *alcohol.*

II.—Acids precipitated by Nitrate of Silver.

96. Hydrochloric Acid. (HCl.)

This acid is a transparent colourless gas, fuming strongly in a moist atmosphere; it has a pungent suffocating smell, and a strongly acid taste. At a low temperature, and under a pressure of about eighteen atmospheres, it becomes liquid: it is decomposed by those metals which decompose water, and by substances which combine with chlorine; it is also decomposed by metallic oxides. It is absorbed with the greatest avidity by water, the saturated solution forming what is called concentrated hydrochloric acid. This solution is colourless and strongly acid; the yellow tinge which the acid frequently has, arises from impurities. The greater number of the chlorides are soluble in water; the principal exceptions are those of *lead* and *silver*, and *subchloride of mercury:* some chlorides volatilize without decomposition, as the chlorides of *tin, antimony,* and *arsenic;* some are fixed, and others undergo decomposition by heat.

Comportment of solutions of Chlorides with reagents.

(Solution of Chloride of Sodium ($NaCl$) may be used.)

Nitrate of silver produces a white curdy precipitate even in highly dilute solutions ($AgCl$), becoming violet-coloured, and finally black, when exposed to the light: it is quite insoluble in nitric acid, but readily soluble in ammonia; it fuses without decomposition, forming, when cold, a tough horny mass, and is reduced by hydrogen, and by fusion with carbonate of soda, or with resin.

Nitrate of suboxide of mercury produces a white precipitate (calomel, Hg_2Cl), becoming black when brought into contact with caustic alkalies.

Acetate of lead produces a white precipitate soluble in boiling water, less so in *nitric* and *hydrochloric* acids, and not altered by ammonia.

By heating a soluble chloride with peroxide of manganese and sulphuric acid, *chlorine gas* is evolved. Thus:—

$$NaCl + MnO_2 + 2(HO,SO_3) = NaO,SO_3 + MnO,SO_3 + Cl + HO.$$

By heating a chloride with sulphuric acid alone, *hydrochloric acid gas* is evolved. Thus:—

$$NaCl + HO,SO_3 = NaO,SO_3 + HCl.$$

On heating a chloride with *chromate of potassa* and sulphuric

acid, a brownish-red gas is disengaged, which condenses into a blood-red liquid.

On the addition of ammonia a yellow liquid (chromate of ammonia) is formed, which becomes red on the addition of an acid, bichromate of ammonia being formed.

Before the blowpipe chlorides are thus detected:—Dissolve oxide of copper in microcosmic salt on platinum wire, until a diaphanous bead is obtained in the oxidizing flame; the substance under examination is now added and heated: if chlorine be present, the assay will be surrounded by a beautiful blue-coloured flame inclining to purple, which after some time disappears, but can be reproduced by adding a fresh supply of the sample.

Characteristic reaction.—That with *nitrate of silver.*

97. Hydrobromic Acid. (HBr.)

General characters.—It very much resembles hydrochloric acid gas; like it, it fumes strongly when allowed to escape into a moist atmosphere, and it acts in a similar manner with metals and metallic oxides: it dissolves freely in water, and the concentrated solution, which is denser than that of hydrochloric acid gas, is fuming; chlorine expels from it bromine, hydrochloric acid being formed. The aqueous solution dissolves a large quantity of bromine, and acquires a deep-red colour. There is also a strong analogy between the bromides and chlorides.

Comportment of solutions of Bromides with reagents.

(Solution of Bromide of Potassium (KBr) may be used.)

Nitrate of silver produces a yellowish-white precipitate (AgBr), insoluble in nitric acid and soluble with difficulty in ammonia.

Nitrate of suboxide of mercury produces a yellowish-white precipitate.

Acetate of lead produces a white precipitate insoluble in water, by which it is distinguished from *chloride of lead.*

Nitric acid, when heated with solution of a bromide, decomposes it, evolving bromine, which colours the solution yellowish-red; when heated with a solid bromide, yellowish-red vapours are produced, having an odour resembling that of chlorine; these vapours condense into red drops in the upper part of the test-tube.

Concentrated sulphuric acid also decomposes bromides, with the separation of *bromine* and *sulphurous acid*. Thus:—

$$KBr + 2(HO,SO_3) = KO,SO_3 + SO_2 + Br + HO.$$

Dilute sulphuric acid decomposes bromides with the disengagement of hydrobromic acid. Thus:—

$$KBr + HO,SO_3 = KO,SO_3 + HBr.$$

If a stream of chlorine be passed through a solution of a bromide, and the solution agitated with *ether*, the latter will dissolve all the evolved bromine, and assume a yellow colour: if the ethereal solution be removed with a pipette, and agitated with solution of potassa, the yellow tint will vanish, the bromine having passed into *bromide of potassium* and *bromate of potassa*. Thus:—

$$6Br + 6KO = 5KBr + KO,BrO_5.$$

If this solution be evaporated to dryness, and ignited, the bromate is decomposed with evolution of oxygen, and bromide of potassium remains; in order to detect bromine in this residue, it is heated in a small retort, with peroxide of manganese and sulphuric acid, and the vapours received in a small receiver containing *starch paste*, which becomes tinged orange-yellow, the colour vanishing by exposure to the air.

On heating a bromide with *chromate of potassa* and *sulphuric acid*, a brownish-red gas is produced, as in the case of a chloride: this gas, however, is *bromine*, and the colour vanishes on the addition of ammonia; this reaction serves, therefore, to distinguish between bromides and chlorides, and for detecting the presence of the latter in the former.

Characteristic reaction.—Those with *nitrate of silver*, with *chlorine*, and with *nitric acid*.

98. Bromic Acid. (HO,BrO_5.)

General characters.—When concentrated, it is very sour, but not caustic; it has very little odour: it first reddens, and then discolours blue litmus-paper; *sulphurous*, *phosphorous* acids, and all the hydracids decompose it, liberating bromine: most of the bromates are soluble in water, and are converted by ignition into bromides, with evolution of oxygen; they are decomposed with violent deflagration when heated with combustible substances, such as *carbon*, *sulphur*, and *phosphorus*. These mixtures likewise detonate violently when moistened with a drop of concentrated sulphuric acid. Bromates, when treated with concentrated sulphuric and other oxygen acids

in the cold, evolve oxygen and red vapours of bromine; they are likewise reduced by sulphuretted hydrogen with separation of sulphur.

Comportment of solutions of Bromates with reagents.

(Solution of Bromate of Potassa (KO, BrO_5) may be used.)

Nitrate of suboxide of mercury produces a light-yellow precipitate, soluble in nitric acid.

Acetate of lead produces a white precipitate, soluble in much water.

Nitrate of silver produces a white precipitate, soluble in ammonia, but soluble with difficulty in dilute nitric acid.

Hydrosulphuric acid reduces bromates to bromides; *sulphuric acid* being formed and sulphur separated.

Sulphurous acid reduces bromates to bromides, sulphuric acid being formed.

99. Hydriodic Acid. (HI.)

General characters.—This acid gas likewise resembles in its properties hydrochloric acid; it is absorbed rapidly, and in large quantities, by water, the solution being colourless and fuming; there is also a strong analogy between the compounds of *iodine* and those of *bromine* and *chlorine*.

Comportment of solution of Iodides with reagents.

(Solution of Iodide of Potassium (KI) may be used.)

Nitrate of silver produces a yellowish-white precipitate (AgI) which blackens by exposure to the light, is insoluble in dilute nitric acid, and very sparingly soluble in ammonia.

Nitrate of suboxide of mercury produces a yellowish-green precipitate.

Chloride of mercury produces a beautiful scarlet precipitate. (HgI.)

Acetate of lead produces an orange-yellow precipitate, soluble in hot water, and in nitric acid, and crystallizing out of its solution in brilliant golden-coloured scales. (PbI.)

Protochloride of palladium produces a black precipitate in solutions of alkaline iodides; no precipitate is afforded by this reagent in solutions of bromides.

An aqueous solution of one part of crystallized sulphate of copper, and two and a half of protosulphate of iron, produce a dingy-white precipitate (Cu_2I); this mixture has no effect in solutions of *chlorides* and *bromides*.

Chlorine, nitric acid, concentrated sulphuric acid, and *peroxide of manganese* eliminate iodine from solutions of iodides, the solutions becoming coloured; and, if the solution be concentrated, *iodine* separates as a black precipitate: on applying heat, the characteristic violet vapours of iodine make their appearance; with excess of chlorine, a colourless *chloride* of iodine is formed.

With *starch paste* free iodine forms a blue compound, and this reagent serves to detect minute traces of iodine in insoluble as well as in soluble compounds of that element. The substance under examination is mixed in a retort with concentrated *nitric acid*, and a strip of *white cotton cloth*, moistened with solution of starch, suspended from the stopper; in a few hours the cloth will become coloured blue if the most minute trace of iodine be present. Nitric acid is better as an oxidizing agent than chlorine, because of the formation of the colourless *chloride of iodine* above referred to. The blue colour of the iodide of starch disappears by heat, and by the action of certain deoxidizing agents.

If a solid iodide be heated with concentrated sulphuric acid and peroxide of manganese, violet vapours of iodine will make their appearance.

Before the blowpipe, metallic iodides, when treated with cupriferous microcosmic salt, impart a beautiful and deep-green colour to the flame. Iodine is soluble in *chloroform*, to which it communicates a beautiful *violet* tint. According to Rabourdin, the presence of iodine may be shown by this test in a liquid in a quantity so small as $\frac{1}{10000}$ part of its weight.

Characteristic reactions.—Those with *protochloride of palladium*; and with *starch*, and *nitric acid*.

100. Iodic Acid. (HO,IO_5.)

General characters.—The aqueous solution of this acid is, when concentrated, very sour: it first reddens, and then destroys the colour of litmus-paper; it oxidizes all metals but *gold* and *platinum*, and detonates violently when heated with combustible substances; with sulphuric, nitric, and phosphoric acid, it forms crystalline compounds, and when mixed with vegetable acids a decomposition of both takes place; *carbonic acid* being liberated, and *iodine* precipitated. The iodates are mostly insoluble in water; the neutral alkaline iodates are soluble.

Comportment of solutions of Iodates with reagents.

(Solution of Iodate of Potash (KO,IO_5) or Iodate of Soda (NaO,IO_5) may be used.)

Nitrate of silver produces a white precipitate, soluble in nitric acid and in ammonia.

Chloride of barium, *chloride of calcium*, and *acetate of lead* give white precipitates, soluble in nitric acid. Iodates, when heated alone, are decomposed into iodides and oxygen; they deflagrate when heated with combustibles: they are decomposed by *protochloride of tin*, *iodine* being separated; the latter may be made evident by adding starch paste.

Hydrosulphuric acid reduces iodates to iodides, *sulphuric* acid and *water* being formed, and *iodine* separated.

101. Hydrocyanic Acid. (HCy.)

General characters.—In its pure, anhydrous state, this acid possesses the following properties. It is colourless, inflammable, very volatile, and possessing a strong odour analogous to that of bitter almonds; its taste is at first cool, then burning and disagreeable. Its specific gravity is 0·6957 at 66°; it boils at 80°; it volatilizes rapidly in the air, producing a degree of cold sufficient (if it be not perfectly anhydrous) to cause it to assume a solid form; it is feebly acid to test-paper; it is one of the most energetic poisons known, one drop being sufficient to destroy an animal of considerable size. It is rapidly decomposed, even in close vessels, becoming darker and darker in colour, and eventually quite black; a trace of sulphuric acid prevents this decomposition from taking place: strong acids cause its elements so to arrange themselves with the elements of water as to produce *formic* acid and *ammonia*. Thus:—

$$\underbrace{HC_2N}_{\text{Hydrocyanic acid.}} + 4HO = \underbrace{NH_4O, C_2HO_3}_{\text{Formiate of ammonia.}}.$$

By distillation the formic acid may be separated, the ammonia remaining in combination with the acid which occasioned the decomposition.

The alkalies are reduced by hydrocyanic acid, their metallic radicals combining with cyanogen, and water being formed. Thus:—

$$KO + HCy = KCy + HO.$$

The metallic cyanides thus formed have an alkaline reaction; they are decomposed gradually when dissolved in water, rapidly

when boiled. *Cyanide of potassium* and *cyanide of sodium* may, however, be heated to redness out of contact of air, without suffering decomposition; but in contact with oxides of *tin*, *lead*, *copper*, and many other metals, they are converted into cyanates, the metals being reduced. Thus:—

$$KCy + 2PbO = KO, CyO + 2Pb.$$

The greater number of the metallic cyanides are insoluble in water; they comport themselves differently under the influence of heat, some being resolved into the metal and cyanogen, as is the case with *cyanide of mercury*, and others into *carbides* and nitrogen. The compounds of cyanogen with gold, silver, and other heavy metals, are not decomposed by dilute, and with difficulty by concentrated nitric acid; hydrochloric acid and sulphuretted hydrogen, however, decompose them easily and completely. The cyanides of *iron*, *cobalt*, *manganese*, and *chromium*, when brought into contact with alkaline cyanides, unite with their cyanogen, forming peculiar salt-radicals, in which the presence of the heavy metal cannot be detected by the usual tests.

Comportment of solutions of Cyanides with reagents.

(Solution of Cyanide of Potassium (K Cy) may be used.)

Nitrate of silver produces a white curdy precipitate (Ag Cy) insoluble in dilute nitric acid, and sparingly soluble in ammonia, easily soluble in cyanide of potassium; leaving pure silver when ignited, and evolving cyanogen, which burns with a peach-coloured flame. When moistened with hydrochloric acid, hydrocyanic acid is disengaged.

Acetate of lead produces a white precipitate (Pb Cy).

Subnitrate of mercury produces, in hydrocyanic acid, a grey precipitate of metallic mercury, cyanide of mercury remaining in solution. Thus:—

$$Hg_2O + HCy = HgCy + Hg + HO.$$

Oxide of mercury dissolves freely in hydrocyanic acid, and alkalies occasion no precipitate in the solution. In no other alkaline fluid can oxide of mercury be held in solution; this reaction serves therefore as a test of the presence of hydrocyanic acid. In the presence of hydrochloric acid, *ammonia* produces a precipitate.

A solution of *protosulphate of iron*, which has been partially oxidized by exposure to the air (magnetic oxide of iron), occasions the formation of *Prussian blue* in solution of an alkaline

hydrocyanate containing free hydrochloric acid; this reaction constitutes an excellent test for hydrocyanic acid, but it is essential that an alkali should be present, as also hydrochloric acid, to dissolve any oxide of iron that may have been precipitated by the alkali together with the blue compound.

A most delicate test of the presence of hydrocyanic acid is that proposed by Liebig, and is dependent on the fact that the higher sulphides of ammonium are instantly deprived, by cyanide of ammonium, of the excess of sulphur they contain above the *monosulphide; sulphocyanide of ammonium* (NH_4, CyS_2) being formed,

$$HCy + NH_4S + S_2 = (NH_4Csy) + HS,$$

which produces, with persalts of iron, a very deep blood-red colour. Taylor recommends the following method of applying this test:—Place the diluted hydrocyanic acid in a watch-glass, and invert over it another watch-glass, holding in its centre one drop of *sulphide* of ammonium containing sulphur in excess; there is no apparent change in the sulphide, but if the watch-glass be removed after the lapse of from half a minute to ten minutes, according to the quantity of hydrocyanic acid present, *sulphocyanide of ammonium* will be obtained. On gently heating the drop of sulphide, and evaporating it to dryness, the addition of a drop of solution of a persalt of iron to the dried residue, brings out the blood-red colour instantly, which is intense in proportion to the quantity of sulphocyanide present; the warmth of the hand may be employed to expedite the evolution of the vapour. This test is even more delicate and expeditious than the nitrate of silver test, in which the vapours are received in a solution of that salt, and will, according to Taylor, detect in five minutes, hydrocyanic acid not exceeding $\frac{1}{4700}$ of a grain, in ten drops of a liquid.

Solid cyanides when heated with concentrated sulphuric acid evolve *carbonic oxide*, sulphate of the metallic base and sulphate of ammonia being formed. Thus:—

$$KC_2N + 2HO + 2HO,SO_3 = NH_4O,SO_3 + KO,SO_3 + 2CO.$$

102. *Detection of Hydrocyanic Acid in Organic Mixtures.*

When hydrocyanic acid is to be sought for in organic mixtures, Taylor urges the importance of obtaining evidence of its presence before resorting to the process of distillation, in order to avoid an objection which may be raised, to the effect that the acid might have been a product of distillation. He gives

the following method, which he finds to succeed with the blood, muscles, and viscera, as well as with the liquid contents and solid substance of the stomach. The liquid is acidulated with sulphuric acid and placed in a wide-mouthed bottle, the aperture of which is capable of being covered with a watch-glass or a saucer of white porcelain. The inside of the glass or saucer is moistened with nitrate of silver and placed over the mouth of the bottle: if hydrocyanic acid be present, the spots of nitrate will become white in the course of a few seconds, or in from ten minutes to a quarter of an hour, according to the quantity of poison present, and the closeness of the test to the liquid. No heat need be applied to the liquid; a temperature of 64° suffices for the result, but the warmth of the hand accelerates the action. Taylor mixed *two-thirds of a grain* of anhydrous hydrocyanic acid with *eight ounces* of porter, and obtained a well-defined deposit of cyanide of silver in the watch-glass in a quarter of an hour; and by substituting in the watch-glass weak caustic potassa for nitrate of silver, and after a few minutes adding sulphate of iron and hydrochloric acid, he obtained Prussian blue from *two-thirds* of a grain of anhydrous hydrocyanic acid mixed with eight ounces of porter; the process was equally successful with the stomach of a dog, after it had been thoroughly washed with water, and had been removed from the body twenty-four hours. These experiments prove the great volatility of the poison, and the diffusibility of its vapour. The silver test serves the analyst as a guide, for Taylor finds, that unless the white film is formed on the nitrate of silver, the application of the Prussian blue test will also fail. Prussian blue may even be procured from the cyanide of silver: for this purpose, caustic potassa is added to the film of cyanide in the watch-glass, and heat applied; the cyanide is dissolved, and brown oxide of silver precipitated; to the filtered liquid sulphate of iron is added, and after a time dilute sulphuric acid, Prussian blue is immediately produced. When it is found necessary to distil the fluid, Lassaigne and Christison acidulate with sulphuric acid, and distil from a vapour bath till one-eighth part of the fluid has passed into the receiver. The tests are then applied to the distillate; if the quantity of poison be small, nitrate of silver, or potassa, may be placed in the receiver to fix the acid as it passes over.

Poisoning by Hydrocyanic Acid.—Liebig makes the following remarks on this fearful poison:—"Its rapid action on the blood

is very remarkable. Comparatively large quantities of the acid in aqueous solution may be taken into the digestive apparatus without producing any very perceptible noxious effects; while the same quantity inhaled as vapour causes immediate death. Thus, a cat can bear the administration of from two to three drops of anhydrous hydrocyanic acid diluted with from four to six ounces of water, without being in the least affected by it. If two drops of the anhydrous acid be inserted into the mouth of the same animal, taking care at the same time to prevent it from breathing by stopping its mouth and nostrils, no perceptible effect is produced; but the cat dies the very instant it is permitted to breathe, and consequently as soon as the vapour of the acid gets into the lungs."

With respect to the quantity of hydrocyanic acid requisite to destroy life, the matured opinion of Taylor is, that a quantity of Scheele's acid (at five per cent.), *above twenty drops* (i. e. *one grain of anhydrous acid*), or an equivalent portion of any other acid, would commonly prove fatal. Even less than this—seven-tenths of a grain—might under favourable circumstances, destroy life. The largest dose from which an adult has been known to recover is *forty minims* at 3¼ per cent., which is equivalent to about a grain and a third of anhydrous acid. It may be well to observe that the acid of commerce differs much in strength, according to the process by which it has been prepared, and independently of decomposition by keeping. The medicinal acid long used in this country was intended to be an imitation of that of Vauquelin, which contains 3·3 per cent.; but the London College of Physicians have improperly (as Dr. Christison observes) altered the strength to 2 per cent.: that of Giese, which keeps well, is of the same strength as the first; that of Schrader contains only 1 per cent; that of Göbel, 2·5 per cent.; that of Ittner, 10 per cent. Of the alcoholic solutions the best known are that of Schrader, which contains about 1·5 per cent. of pure acid; that of the Bavarian Pharmacopœia, which contains 4 per cent.; that of Duflos, 9 per cent.; that of Pfaff, 10 per cent.; and that of Keller, 25 per cent. The medicinal dose is from a minim to two minims of Scheele's acid, and from three to five minims of the London Pharmacopœial acid gradually increased.

Every grain of anhydrous acid yields 5 grains of cyanide of silver. Suppose 100 grains of a sample to have yielded 45

grains of cyanide, it follows that the acid contains 9 grains of anhydrous acid to 91 grains of water. To procure an acid containing 2 per cent. of anhydrous acid, would require the addition of 9 grains of anhydrous acid to 441 grains of water; now, as the acid in question contains already 91 grains of water in every 100 grains, it is evident that we need only add 350 grains of water to every 100 grains of the acid, in order to prepare an acid of 2 per cent. strength ($441-91=350$).

103. Hydrosulphocyanic Acid. ($HCyS_2$.)

The sulphocyanides, most of which are soluble both in water and in alcohol, are recognized by the following reactions:—

Nitrate of silver produces a white precipitate ($AgCyS_2$), insoluble in dilute nitric acid, and in ammonia, and furnishing metallic silver when ignited.

Sesquichloride of iron gives an intense blood-red colour; if the red liquor be acidulated with hydrochloric acid, and fragments of zinc added, sulphuretted hydrogen is evolved and the colour disappears.

A mixture of *protosulphate of iron with a salt of copper*, occasions a white precipitate.

Subnitrate of mercury gives a white precipitate.

Sulphocyanide of sodium (or of *ammonium*) exists in the saliva, and may be detected by allowing a little dilute solution of perchloride of iron to remain for a few seconds in the mouth: on expelling it, it will be found to have acquired a distinct red tinge.

104. Hydroferrocyanic Acid. (H_2Cy_3Fe; or H_2Cfy.)

This acid, when exposed to the air, absorbs oxygen and becomes blue; its solution when boiled is decomposed into hydrocyanic acid and a white compound, which becomes blue by exposure to the air. With alkalies it forms salts which are soluble in water; most of the other ferrocyanides are insoluble.

Comportment of soluble Ferrocyanides with reagents.

(Solution of Ferrocyanide of Potassium ($KCfy$) may be used.)

Protosulphate of iron produces a pale-blue precipitate. (*See* Protoxide of Iron.)

Sesquichloride of iron, a deep-blue precipitate (Prussian blue. (*See* Sesquioxide of Iron.)

Sulphate of copper a reddish-brown precipitate (Cu_2Cfy).

Protonitrate of cobalt a yellowish-green precipitate.

With salts of *zinc, lead, silver,* and *mercury,* white precipitates.

Insoluble ferrocyanides are decomposed by fusion with alkaline carbonates, soluble alkaline ferrocyanides being formed. When an alkaline ferrocyanide is distilled with dilute sulphuric acid, hydrocyanic acid is formed; but if it be heated with excess of concentrated sulphuric acid carbonic acid is formed by the following reaction:—

$$K_2FeC_6N_3, + 9HO = 6CO + 2KO + FeO + 3NH_3.$$

One equivalent of ferrocyanide of potassium and nine equivalents of water from the oil of vitriol and the water of crystallization of the ferrocyanide, give rise to six equivalents of carbonic oxide, two equivalents of potassa, one of protoxide of iron, and three of ammonia; the sulphuric acid, oxide of iron, potassa, and ammonia arrange themselves into a crystalline anhydrous iron alum, having the following composition (Fownes):—

$$2(Fe_2O_3, 3SO_3) + \left.\begin{matrix} KO, SO_3 \\ NH_4O, SO_3. \end{matrix}\right\}$$

105. HYDROFERRIDCYANIC ACID. ($H_3Cy_6Fe_2$; or H_3Cfdy.)

The potassium compound of this acid is obtained by passing a current of chlorine through a solution of ferrocyanide of potassium, until the liquid ceases to give a precipitate with sesquichloride of iron. Ferridcyanide of potassium is formed by the following reactions:—

$$2(K_2Cy_3Fe) + Cl = (K_3Cy_6Fe_2) + KCl.$$

The alkaline ferridcyanides have a red colour; that of potassium crystallizes in fine right-rhombic prisms.

Protosulphate of iron produces with ferridcyanide of potassium a fine blue colour (Turnbull's blue).

$$K_3(Cy_6Fe_2) + (3FeO, SO_3) = Fe_3(Cy_6Fe_2) + 3(KO, SO_3).$$

Sesquichloride of iron occasions no precipitate but only gives a darker colour to the solution.

Sulphate of copper produces a yellowish-green precipitate.

Protonitrate of cobalt a dark reddish-brown precipitate.

Nitrate of silver produces a dark orange-coloured precipitate soluble in ammonia.

Subnitrate of mercury a brownish-red precipitate. The insoluble ferridcyanides are decomposed by fusion with alkaline carbonates, soluble ferridcyanides being formed.

106. HYDROSULPHURIC ACID (SULPHURETTED HYDROGEN). (HS.)

This acid is a colourless gas, which under strong pressure becomes liquid; it has a highly offensive odour, resembling that of putrid eggs; its taste is acid, astringent, and bitter; it is inflammable, burning with a blue flame, and disengaging sulphurous acid; it explodes violently when mixed with oxygen or atmospheric air and ignited; when mixed with chlorine, sulphur is deposited and hydrochloric acid formed; it is highly deleterious when inspired, even when mixed with a large quantity of air; it is absorbed by water, which acquires its peculiar smell and a nauseous sweet taste; the solution reddens litmus-paper, and decomposes by exposure to the air, sulphur being deposited; most metallic oxides are decomposed by *hydrosulphuric acid*, *sulphides of the metals*, and *water*, being formed. The *alkalies* and *alkaline earths*, and the oxides of *chromium*, *tantalum*, and *titanium*, do not exchange their oxygen for sulphur in the moist way. The sulphides of the metals of the alkalies, and the alkaline earths, are soluble in water; they are decomposed by dilute mineral acids with the evolution of sulphuretted hydrogen, which is readily recognized by its odour and by its action on paper moistened with solution of lead.

$$KS + HO,SO_3 = KO,SO_3 + HS.$$

The sulphides of the metals of the fourth group are insoluble in water, but are likewise decomposed by dilute mineral acids.

$$FeS + HO,SO_3 = FeO,SO_3 + HS.$$

All the other metallic *sulphides* but *sulphide of mercury* are decomposed by strong nitric acid, sulphuric acid being formed, and sulphur generally separated; aqua-regia effects their decomposition more easily, it also dissolves sulphide of mercury. As some metallic oxides, when dissolved in acids, are precipitated by sulphuretted hydrogen, while others are not, and as the precipitated sulphides differ in colour, and in other properties, sulphuretted hydrogen becomes a valuable reagent for detecting and separating metallic compounds. Most metallic sulphides are decomposed by heat with access of air, evolving sulphurous acid; the alkaline sulphides thus treated are converted into sulphates.

When hydrosulphuric acid, or a solution of an alkaline or earthy sulphide, is brought into contact with *nitrate of silver* or *acetate of lead*, black precipitates are formed.

$$AgO,NO_5 + HS = AgS + HO,NO_5.$$

$$PbO,\bar{A} + HS = PbS + HO,\bar{A}.$$

Either of these salts are therefore certain tests of the presence of this acid in the gaseous state; a strip of paper moistened with solution of subacetate of lead is generally employed.

Chlorine, *bromine*, *sulphurous acid*, *nitrous acid*, *iodic acid*, *chromic acid*, and the *sesquisalts of iron* all decompose *hydrosulphuric acid* with the separation of sulphur.

An alcoholic solution of *iodine* (or an aqueous solution of iodine in iodide of potassium) is converted by hydrosulphuric acid into hydriodic acid with the separation of sulphur.

$$I + HS = HI + S.$$

All the compounds of sulphur when mixed with soda and ignited on charcoal before the blowpipe in the reduction flame, yield *liver of sulphur*, which evolves sulphuretted hydrogen when treated with a mineral acid, and produces a brownish-black spot, when moistened and placed on a piece of polished silver.

III.—Acids not precipitated by either Chloride of Barium or Nitrate of Silver.

107. Nitric Acid. (NO_5.)

General characters.—This acid has been obtained in an anhydrous state by passing perfectly dry chlorine gas over crystals of well-dried nitrate of silver at a temperature not exceeding 200° Fahr. The hydrated acid, in its most concentrated form, is a colourless, fuming liquid, very easily decomposed, mere exposure to the light causing it to become yellow, and to disengage oxygen gas. It is one of the strongest of the acids, and constitutes a reagent of the greatest value, from the facility with which it parts with a portion of its oxygen. The yellow fuming acid, containing nitrous acid, possesses generally the greatest oxidizing power. The most highly concentrated acid is, in many cases, without action on bodies on which a diluted acid acts with energy; thus the concentrated acid does not attack *lead* or *tin*, while the addition of a small quantity of water causes an energetic action to take place. Organic substances are for the most part resolved by the concentrated acid into carbonic acid and water, the action in many cases being sufficiently energetic to cause them to take fire; the diluted acid generally converts them into oxalic, malic, and carbonic acids. Nearly all metallic oxides are dissolved by nitric acid, the exceptions are oxides of *tin* and *antimony*, *tellurous* and *tungstic acids*. All the neutral salts of nitric acid are soluble

in water, and all are decomposed at a strong red-heat, the nature of the products depending on the nature of the base; thus the alkaline nitrates yield oxygen and nitrogen, while other metallic nitrates give oxygen and an inferior oxide of nitrogen. When nitrates are ignited in the presence of other substances susceptible of oxidation, they take the liberated oxygen, and in some cases the combination is attended by deflagration; thus a nitrate thrown on red-hot charcoal causes the latter to throw off brilliant scintillations; a mixture of a nitrate with cyanide of potassium deflagrates vividly when heated on a platinum plate; and phosphorus and sulphur brought into contact with a heated nitrate, occasion a violent detonation.

108. *Detection of Nitric Acid in solutions of Nitrates.*

(Solution of Nitrate of Potash (KO,NO_5) may be used.)

Hydrochloric acid added in excess to nitric acid or to a solution of a nitrate, gives it the property of dissolving gold leaf, in consequence of the liberation of chlorine.

When a solution containing a nitrate is mixed with half its volume of concentrated sulphuric acid, allowed to cool, and a crystal of *protosulphate of iron* added, the liquid round the crystal assumes a reddish-brown colour, in consequence of the following reaction.

$$10(FeO,SO_3) + KO,NO_5 + 4(HO,SO_3) =$$
$$4(FeO,SO_3),NO_2 + 3(Fe_2O_3,3SO_3) + KO,SO_3 + 4HO.$$

Or, the solution to be tested having been mixed with a larger volume of concentrated sulphuric acid and allowed to cool, a strong solution of protosulphate of iron is carefully poured upon it, when a *violet amethystine-red* or *blackish-brown* colour, according to the quantity of nitric acid present, will be seen at the place of contact, which increases on careful agitation, but disappears on heating. By this mode of operating, and in the absence of chlorine, the smallest traces of nitric acid may be detected.

When a solution of a nitrate is concentrated, and heated in a test-tube with copper filings or turnings, and concentrated sulphuric acid, nitric oxide gas is set free, which, combining with the oxygen of the air in the tube, forms ruddy fumes of *hyponitric acid.*

$$(1.)\ KO,NO_5 + HO,SO_3 = KO,SO_3 + HO,NO_5.$$
$$(2.)\ 4(HO,NO_5) + 3Cu = 3(CuO,NO_5) + 4HO + NO_2.$$

When a solution of a nitrate is mixed with sulphuric acid,

and a sufficient quantity of a solution of indigo in sulphuric acid added to give it a distinct blue colour, and the mixture heated, the colour is either discharged, or turned yellow, in consequence of the oxidation of the indigo at the expense of the nitric acid.

If a small crystal of *sulphate of manganese* be placed in a porcelain capsule, covered with phosphoric acid, and heated to dryness, a colourless residue is obtained; but if the smallest quantity of nitric acid, or a nitrate be present, it has a *violet*, *crimson*, or *dark-red* colour, according to the quantity of nitric acid. This is probably the most delicate test of this acid at present known.

If a solid nitrate be heated with concentrated sulphuric acid, nitric acid distils over, which produces a white cloud with ammonia, and does not occasion any turbidity when passed into solution of nitrate of silver; sometimes the brownish-red fumes of hyponitric acid are perceptible, in consequence of the decomposition of nitric acid by the heat.

All nitrates when heated on charcoal deflagrate; *violently* with *cyanide of potassium*, in consequence of the decomposition of the cyanogen, carbonic acid and nitrogen being evolved.

109. Nitrous Acid. (NO_3.)

At ordinary temperatures this acid is a gas of a dark yellowish-red colour; at 0° Fahr. it condenses into a blue and very volatile liquid, which is decomposed when brought into contact with water. Thus:—

$$3NO_3 + HO = HO,NO_5 + 2NO_2.$$

Nitrous acid forms a class of salts called *nitrites*. The alkaline *nitrites* are soluble in alcohol; the corresponding nitrates are insoluble.

When submitted to gentle distillation, the *nitrites* expel nitric oxide gas, *nitrates* being formed.

The neutral nitrites colour the protosalts of iron a blackish-brown.

They reduce *terchloride of gold* and *subsalts of mercury* to the metallic state.

With *nitrate of silver* alkaline nitrites produce a sparingly soluble crystalline *nitrite of silver*.

When a fragment of nitrite of potash is moistened with a solution of sulphate of copper, a *brilliant-green colour* is produced.

Acetic acid decomposes solutions of nitrites, the liquid then

striking an *olive-green* colour with solution of *protosulphate of iron.*

110. Chloric Acid. (HO,ClO_5.)

When concentrated, it is a yellowish oily-looking liquid, very sour, reddening, and finally bleaching, litmus-paper; it is very unstable, being resolved by heat into *perchloric acid, oxygen,* and *chlorine:* it converts sulphurous into sulphuric acid, and is at the same time itself reduced to chlorine; it also converts sulphuretted hydrogen into sulphuric acid, sulphur, and water; all its compounds with bases, are soluble in water; they do not possess bleaching properties, but when mixed with sulphuric acid they are decomposed, perchloric acid, chlorine, hypochloric acid, and oxygen being formed; the solution becomes yellow, and it then possesses the power of destroying the colour of blue vegetable infusions, and by the application of heat decolorizes solution of indigo. The alkaline *chlorates,* when ignited, disengage oxygen, and become converted into *chlorides;* most other chlorates are resolved by heat into metallic oxides, and a mixture of oxygen and chlorine. Concentrated sulphuric acid in contact with the chlorates, is coloured, first brown and then yellow, whilst a very explosive greenish-yellow gas (ClO_4) escapes.

$$3(KO,Cl_5O)+4(HO,SO_3)=$$
$$2(KO,HO,2SO_3)+KO,ClO_7+2ClO_4+2HO.$$

When triturated with sulphur or phosphorus, chlorates detonate with dangerous violence; a mixture of a chlorate with sugar bursts into a flame on being touched with a drop of concentrated sulphuric acid.

The compounds of *perchloric acid* (HO,ClO_7) with bases, are distinguished from chlorates by their greater stability, not being decomposed by acids or reducing agents; their solutions do not therefore become yellow on being mixed with sulphuric acid. The *perchlorate of potassa* is remarkable for its difficult solubility in water.

The compounds of *hypochloric acid* (ClO) with bases have bleaching properties. Bleaching salts (*hypochlorite of lime* and *hypochlorite of soda*) are always mixed with *chlorides. Chloride of lime* contains also some hydrate of lime. They are decomposed on the addition of an acid, with the evolution of chlorine only.

$$CaO,ClO+CaCl+2(HO,SO_3)=2(CaO,SO_3)+2Cl+2HO.$$

They are powerful oxidizing agents, and are decomposed by heat and by exposure to light; they decompose salts of *manganese*, and *lead*, precipitating from the former, hydrated peroxide of manganese, and from the latter, first chloride, and then brown peroxide.

Pure hypochlorites, when treated with sulphuric acid, evolve hypochlorous acid.

$$CaO,ClO + HO,SO_3 = CaO,SO_3 + ClO + HO.$$

If a solution of arsenious acid in hydrochloric acid be coloured blue by solution of indigo, and mixed gradually with a dissolved bleaching salt, no decolorization of the liquid will take place until all the arsenious acid has been converted into arsenic acid. On this reaction is founded a method of estimating the value of bleaching-powder.

B.—ORGANIC ACIDS.

I.—Acids precipitated by Chloride of Calcium.

(*Oxalic, Tartaric, Paratartaric, Citric, and Malic Acids.*)

111. Oxalic Acid. (HO,C_2O_3; or $HO,\bar{O}$.)

General characters.—It crystallizes in four-sided prisms, which are colourless, very soluble in water, very acid, and poisonous. These crystals contain three equivalents of water of crystallization, which when sharply heated they lose, the dry acid subliming; at a high temperature, oxalic acid is decomposed into *water*, *carbonic*, and *formic acids*, without blackening, by which it is distinguished from most other organic acids. The alkaline oxalates are soluble in water, as are also some other oxalates with a metallic base; they are all decomposed at a red-heat, alkaline and earthy oxalates being thereby converted into carbonates.

Comportment of solutions of Oxalic Acid, and Oxalates, with reagents.

(Solution of Oxalate of Ammonia ($NH_4O\bar{O}$) may be used.)

Chloride of calcium and all soluble lime salts produce a white precipitate even in highly dilute solutions ($CaO,\bar{O} + 2aq$), insoluble in water as well as in oxalic and acetic acids, but readily soluble in hydrochloric and in nitric acids; the presence of ammonia promotes the precipitation of oxalic acid by salts of lime.

Chloride of barium produces a white precipitate ($BaO,\overline{O} + aq$) almost insoluble in water, but soluble in nitric and in hydrochloric acids.

Nitrate of silver gives a white precipitate, soluble in nitric acid and in ammonia.

Acetate of lead produces a white precipitate.

When heated with concentrated sulphuric acid, oxalic acid and dry oxalates are decomposed, and the oxalic acid resolved into carbonic acid and carbonic oxide gases,

$$HO,C_2O_3 = CO_2 + CO + HO,$$

which escape with effervescence. The latter gas may, if present in sufficient quantity, be kindled; it burns with a blue flame: if the mixture become black, it is a proof that it contains some other organic substance.

112. TARTARIC ACID. ($2HO,C_8H_4O_{10}$; or $2HO,\overline{T}$.)

General characters.—This acid crystallizes in large rhombic prisms, which are soluble in water and have a pleasant acid taste; the solution decomposes by keeping, becoming covered with a mouldiness. When heated, the crystallized acid loses water, and gives rise to the formation of a series of new compounds; and when treated at a high temperature with a strong solution of *hydrate of potassa*, it is converted into *acetate* and *oxalate* of potassa. Thus:—

$$\underbrace{2HO,C_8H_4O_{10}}_{\text{Tartaric acid.}} = \underbrace{HO,C_4H_3O_3}_{\text{Acetic acid.}} + \underbrace{2(HO,C_2O_3)}_{\text{Oxalic acid.}}.$$

The alkaline tartrates are soluble in water; all the salts of tartaric acid that are insoluble in water are easily soluble in hydrochloric acid.

Comportment of Tartaric Acid, and solutions of Tartrates, with reagents.

(Solution of Tartrate of Soda ($2NaO,\overline{T}$) may be used.)

Chloride of calcium produces a white precipitate almost insoluble in water, but soluble in ammoniacal salts, the presence of which, therefore, prevents its formation; it is soluble also in cold potassa, but excess must be avoided, or hydrate of lime will be precipitated; if the potassa solution be boiled, *tartrate of lime* separates as a gelatinous mass, which redissolves as the solution cools.

Lime water produces in solutions of neutral tartrates a white

precipitate, dissolving in tartaric acid, and also in ammoniacal salts.

Chloride of barium produces a white precipitate soluble in dilute acids.

Acetate of lead occasions a white precipitate of tartrate of lead, which when ignited out of access of air is decomposed, metallic lead in a fine state of division being formed, which burns when projected into the air.

Nitrate of silver produces a white precipitate of tartrate of silver, which by boiling is reduced to a shining mirror, adhering to the glass by agitation; the reduced metal separates in thin laminæ.

When a salt of *potassa* (the acetate answers best) is added to free tartaric acid, and the mixture agitated, a sparingly soluble crystalline *bitartrate of potassa* separates; the addition of alcohol further diminishes the solubility of this salt, which is freely dissolved in alkalies and in mineral acids.

Tartaric acid possesses the property of preventing the precipitation of several metallic oxides by alkalies, in consequence of the formation of soluble tartrates not decomposed by alkalies; among the metallic oxides which it thus affects are *alumina, peroxide of iron,* and *protoxide of manganese.*

Tartrates, when heated, carbonize, emitting a very peculiar odour; the tartrates of the alkalies and alkaline earths are thus converted into carbonates.

Paratartaric Acid, or Racemic Acid.

This acid is isomeric with tartaric acid, from which it is distinguished by the insolubility of its *lime salt* in excess of acid and in ammoniacal salts, and by the formation after a time, of a precipitate, with solution of *gypsum.*

113. Citric Acid. ($3HO, C_{12}H_5O_{11}$; or $3HO, \overline{Ci}$.)

General characters.—This acid forms large transparent crystals, very soluble in water, and of a strong but pleasant acid taste; its solution, like that of tartaric acid, decomposes by keeping. The acid itself carbonizes when heated to redness, emitting a pungent acid vapour; when heated with sulphuric acid in excess, it is decomposed into *carbonic acid, carbonic oxide, acetic acid,* and water. Thus:—

$$C_{12}H_5O_{11} + 3HO = 2CO_2, + 2CO, + 2(C_4H_3O_3), + 2HO.$$

The alkaline citrates are soluble in water; the insoluble salts

of citric, and in fact of all organic acids are decomposed by boiling with carbonate of soda, soluble alkaline salts being thus obtained.

Comportment of Citric Acid, and solutions of soluble Citrates with reagents.

(Solution of Citrate of Soda ($3NaO,\overline{Ci}$) may be used.)

Chloride of calcium produces, in solutions of citrates, but not in citric acid, a white precipitate of neutral citrate of lime, insoluble in potassa, but readily soluble in sal-ammoniac, from which, however, a basic citrate of lime is precipitated by boiling.

Lime water produces no precipitate in the cold; but by boiling, basic citrate of lime is deposited, which is redissolved as the solution cools; this reaction serves to distinguish *citric acid* from most other organic acids.

Acetate of lead produces a white precipitate, sparingly soluble in ammoniacal salts and in ammonia, but readily soluble in citrate of ammonia.

Citric acid, like *tartaric acid*, prevents the precipitation of certain metallic oxides by alkalies.

114. Malic Acid. ($2HO, C_8H_4O_8$; or $2HO,\overline{M}$.)

This acid, which occurs in several acid fruits, crystallizes with some difficulty, and deliquesces rapidly when exposed to the air; at the temperature of 230° it gradually decomposes into *fumaric acid* ($2HO,C_8H_2O_6$,), crystallizing in micaceous scales; at a higher temperature it is in a great measure converted into *maleic* acid ($2HO,C_8H_2O_6$,), which rises as a crystalline sublimate, *fumaric acid* remaining in the retort. The salts which this acid forms with bases are mostly soluble in water.

Comportment of Malic Acid, and solutions of Malates with reagents.

Chloride of calcium does not produce any precipitate till alcohol is added, when white *malate of lime* is deposited.

Lime water produces no precipitate either in hot or cold solutions of malates, by which this acid is distinguished from *tartaric*, *racemic*, *citric*, and *oxalic* acids.

Acetate of lead produces a white precipitate ($2PbO,C_8H_4O_8,6aq$), which, by repose, crystallizes in needles, and which

fuses under the boiling-point of water. The best test of malic acid is probably its comportment under heat.

II.—Acids precipitated by Sesquichloride of Iron.

(*Succinic, Benzoic, Tannic, and Gallic Acids.*)

115. Succinic Acid. ($2HO,C_8H_4O_6$; or $2HO,\overline{Su}$.)

This acid is crystalline and volatile; its vapour is exceedingly acrid and penetrating. It is very stable, resisting the action of nitric acid, chlorine, and even of a mixture of hydrochloric acid and chlorate of potash. It combines with anhydrous sulphuric acid, forming *sulphosuccinic acid*, which is tribasic. It was originally obtained from *amber*, whence its name. The salts which it forms with bases are mostly soluble in water.

Comportment of Succinic Acid and solutions of Succinates with reagents.

(Solution of Succinate of Ammonia ($2NH_4O,C_8H_4O_6$) may be used.)

Sesquichloride of iron produces a brownish-red voluminous precipitate, soluble in acids and decomposed by ammonia, hydrated sesquioxide of iron being formed.

Acetate of lead produces a white precipitate of succinate of lead, soluble in excess and in *tartaric* and *acetic acids*.

As the alkaline and earthy succinates are insoluble in alcohol, the acid after the addition of alcohol and ammonia is precipitated by *chloride of barium*.

116. Benzoic Acid. ($HO,C_{14}H_5O_3$; or $HO,\overline{Bz}$.)

This acid is obtained by sublimation, in the form of light flexible pearly scales, or by precipitation as a crystalline powder. When pure, it has no smell. It is fusible and volatile, its vapour being like that of succinic acid, very irritating. It is not very soluble in cold water, more so in hot, and readily soluble in alcohol. Its principal source is *gum-benzoin*. Most of its salts are soluble in water.

Comportment of Benzoic Acid and solutions of Benzoates with reagents.

(Solution of Neutral Benzoate of Ammonia ($NH_4O,C_{14}H_5O_3$) may be used.)

On the addition of hydrochloric acid to the solution of a benzoate in water, benzoic acid separates as a white crystalline powder.

Sesquichloride of iron produces a pale-yellow precipitate, decomposed by ammonia, and by strong acids, which combine with sesquioxide of iron, benzoic acid being precipitated.

Acetate of lead does not immediately precipitate free benzoic acid; but it produces a white flaky precipitate in solutions of fixed alkaline benzoates.

117. Tannic Acid. ($C_{54}H_{22}O_{34}$, *Strecker.*)

When pure, this acid is nearly white, but not at all crystalline. It is very soluble in water; the solution absorbs oxygen from the air, and is converted into *gallic* acid. It has a most astringent but not bitter taste. It is almost insoluble in ether. It is obtained in a state of purity from the *gall nut*, of which it constitutes nearly two-thirds of the weight. On the addition of a mineral acid, a precipitate composed of tannic acid, and the acid employed, is determined. Solution of *gelatine* produces an insoluble curdy precipitate. The whole of the tannic acid in a solution may be removed by a piece of animal membrane.

Solution of starch, and most of the vegetable bases also, produce precipitates.

Sesquichloride of iron gives a dark blue-black precipitate.

118. Gallic Acid. ($3HO, C_{14}H_3O_7 2aq$, *Strecker.*)

This acid forms beautiful prisms of a silky lustre, and a slightly yellow colour. It is not very soluble in cold, but dissolves in three parts of boiling water. Its alkaline solution, when exposed to the air, becomes first yellow, then green, red, brown, and finally nearly black, by the absorption of oxygen. It is *not* precipitated by gelatine; its solution in hot sulphuric acid is precipitated by water as a reddish-brown, crystalline powder, possessing colouring properties, and which, when heated, yields fine red prisms. By the action of heat it is converted into pyrogallic and metagallic acids.

Solutions of *gallic acid* give, with a mixture of the salts of *protoxide* and *sesquioxide of iron*, a dark-blue precipitate; with salts of *oxide of iron* the precipitate is black.

III.—Acids not precipitated by Chloride of Calcium, or by Sesquichloride of Iron.

(*Acetic, Formic, Uric, and Meconic Acids.*)

119. Acetic Acid. ($HO,C_4H_3O_3$; or HO,AcO_3; or $HO,\bar{A}$.)

The normal acid at temperatures below 60° is a crystalline solid. It melts at 62° or 63°, forming a liquid of a pungent, peculiar, and agreeable smell, and a burning acid taste. It has a powerful action on the skin, on which it raises a blister, producing a painful sore. It boils at 248°, and its vapour is inflammable. It is decomposed by anhydrous sulphuric acid, and also by chlorine, two new acids, *sulphacetic* and *chloracetic acids*, being formed. It is also decomposed when passed in a state of vapour through a red-hot tube, the products being *carbonic acid* and *acetone.* Thus:—

$$C_4H_3O_3 = CO_2 + \underbrace{C_3H_3O}_{\text{Acetone.}}$$

Acetates, when heated, are decomposed with the same transformation. The greater number of the acetates are soluble in water. *Acetate of silver*, and acetate of *suboxide of mercury* are crystalline, and only sparingly soluble. When heated with dilute sulphuric acid, acetates are decomposed with the liberation of acetic acid; when heated with concentrated sulphuric acid and alcohol, *acetic ether* is disengaged, which may be known by its peculiar odour. When an acetate is heated with *potassa* and *arsenious* acid, *oxide of kakodyl* (C_4H_6As,O) highly poisonous, is disengaged. With excess of oxide of lead, acetic acid forms a solution which has an alkaline reaction. *Sesquichloride of iron* exhibits no reaction with acetic acid; but in solutions of neutral acetates, peracetate of iron is formed, which imparts to the solution a blood-red colour.

120. Formic Acid. (HO,C_2HO_3.)

This acid in its most concentrated state, fumes in the air, and has a very pungent acid smell. At a low temperature, it crystallizes in brilliant scales. It is highly corrosive, acting powerfully on the skin, and producing painful sores. It boils at 212°, and its vapour is inflammable; all its salts are soluble in water. They have a general resemblance to the acetates, but are, nevertheless, quite distinct. When heated to redness, they give off

carbonic acid and carbonic oxide, leaving the metal reduced, or carbonic oxide, leaving a metallic oxide. By the property which this acid and its salts possess, of reducing the oxides of the precious metals, it is distinguished from acetic acid. When *nitrate of silver*, or *subnitrate of mercury* are added to concentrated solutions of alkaline formiates, sparingly soluble precipitates are formed, and on the application of heat, a reduction instantly takes place, carbonic acid and water being formed. Thus:—

$$HO,C_2HO_3 + 2HgO = 2Hg + 2CO_2 + 2HO.$$

By gently heating chloride of mercury with an alkaline formiate, it is reduced first to subchloride, and then to metallic mercury.

When formic acid is heated with concentrated sulphuric acid, it is decomposed into water and carbonic oxide. Thus:—

$$HO,C_2HO_3 + HO,SO_3 = 2CO + HO,SO_3 + 2HO.$$

The sulphuric acid withdraws from the formic acid the elements of water, and a transposition of its atoms takes place. The same decomposition occurs, on heating a formiate with sulphuric acid.

121. Uric Acid. ($2HO,C_{10}H_2N_4O_4$.)

This acid is separated from its compounds by mineral acids as a white crystalline powder. It is very sparingly soluble in water, the solution reddens litmus; all its salts are likewise very sparingly soluble. When uric acid is dissolved in *nitric* acid, the solution evaporated to dryness, and *ammonia* added, a beautiful *crimson* colour is obtained. This is the characteristic test for uric acid:—the substance to be examined is warmed in a watch-glass with a drop of nitric acid, and evaporated to dryness at a gentle heat; the residue will have a *red* colour if uric acid be present, becoming *crimson* when exposed to the vapour of ammonia. This beautiful compound is *murexid* or *purpurate of ammonia;* on the addition of a drop of caustic potassa a magnificent *purple* colour is produced, which vanishes on the application of heat. By fusion with alkalies, uric acid disengages ammonia.

122. Meconic Acid. ($3HO,C_{14}HO_{11}$, 6aq.)

This acid, which is found only in opium, crystallizes, when pure, in the form of beautiful white silvery scales. It is soluble in water and in alcohol. The solution is decomposed by

boiling; it is also decomposed by hydrochloric acid, and entirely so when heated with excess of *potassa; oxalic acid, carbonic acid*, and a *colouring matter* being the products. Its distinguishing character is that of causing a deep *blood-red colour* in solutions of *persalts of iron*, without, however, any precipitation taking place.

CHAPTER V.

ON THE COMPORTMENT OF THE PRINCIPAL ALKALOIDS WITH REAGENTS.

Nicotina or *Nicotine*, the poisonous alkaloid of *Tobacco*.
Conia or *Conicine*, the poisonous alkaloid of *Hemlock*.
Morphia or *Morphine*, *Narcotina* or *Narcotine*, *Codeia* or *Codeine*, } the alkaloids of *Opium*.
Strychnia or *Strychnine*, *Brucia* or *Brucine*, } the poisonous alkaloids of *Nux vomica*.
Aconitina or *Aconitine*, the poisonous alkaloid of *Monkshood*.
Atropia or *Atropine*, the poisonous alkaloid of the *Deadly Nightshade*.

123. NICOTINA. ($C_{10}H_7N$.)

General characters.—It is a colourless oily liquid, which by exposure to the air becomes first yellow, then brown, and finally solid, by absorbing oxygen. It is inflammable, has an acrid taste, and an extremely irritating odour. It is soluble in water, in alcohol, and in ether; its solution in alcohol turns turmeric-paper brown. Its salts are soluble in water, and in alcohol, but only very sparingly soluble in ether.

Reactions with reagents.

Terchloride of gold produces in aqueous solutions a reddish-yellow precipitate.

Bichloride of platinum causes a yellow precipitate.

Infusion of galls, a copious white precipitate.

Chloride of mercury, *protochloride of tin*, and *acetate of lead*, white precipitates.

Chlorine gas decomposes nicotina with the evolution of hydrochloric acid gas, and the formation of a blood-red liquid, which, on exposure to the rays of the sun, becomes colourless.

Solution of iodine produces with solution of nicotina a

reddish-brown precipitate, the colour of which is destroyed by potassa and by ammonia. The volatility of nicotina is its most marked test.

124. Conia. ($C_{16}H_{15}N$.)

General characters.—This alkaloid is likewise a volatile, oily, colourless liquid, becoming yellow by exposure to the air. It has a powerful odour, like that of fresh *hemlock*. It is very soluble in alcohol and ether, but sparingly so in water. Its vapour fumes when brought into contact with vapours of nitric, hydrochloric, and acetic acids. Its reactions with reagents are very similar to those of *nicotina*, from which it is distinguished by its odour and by its sparing solubility in water.

125. Morphia. ($C_{34}H_{19}NO_6$, + 2aq.)

General characters.—This alkaloid occurs in small, colourless, rectangular prisms; by heat the two equivalents of water which it contains are expelled, and the alkaloid fuses into a resinous mass which on cooling crystallizes. It is soluble in about 1000 times its weight of *cold*, and in about 400 times its weight of *hot* water; the solution has a bitter taste, and an alkaline reaction. It is sparingly soluble in cold alcohol, but abundantly so in hot. In ether it is very sparingly soluble; the fixed alkalies dissolve morphia in considerable quantities, ammonia dissolves it less readily. The salts of morphia are soluble in water and alcohol, especially in presence of excess of acid, but insoluble in ether.

Reactions with reagents.

Nitric acid produces with morphia, or its salts, a dark-*orange* colour, gradually passing into a *yellow*.

A mixture of *nitric and sulphuric acids* colours morphia *green*.

On adding the alkaloid or one of its salts to a solution of *iodic acid*, *iodine* is set free, imparting a *brown* colour to the liquid; if some *starch* be previously added to the iodic acid, the colour becomes *blue*.

Sesquichloride of iron produces a *blue* precipitate, soon passing into a dingy *green*, and finally to a *brown*.

Bichloride of platinum produces a granular *orange-yellow* precipitate.

From a solution of *terchloride of gold* the metal is gradually reduced.

126. Narcotina. ($C_{46}H_{25}NO_{14}2aq.$)

This alkaloid, which crystallizes in large, lustrous, right rhombic prisms, possesses a very feeble alkaline reaction; its salts are all acid, and have a very bitter taste. It is nearly insoluble in water, but abundantly so in alcohol and in ether, especially in the latter, by which property, and by its not striking a blue colour with *sesquichloride of iron*, narcotina is distinguished from morphia. The most characteristic test is however the following:—

If a crystal of narcotina, or of either of its salts, be placed in concentrated sulphuric acid, and a drop of nitric acid added, a *blood-red* colour will be produced, which on the addition of more nitric acid disappears.

127. Strychnia. ($C_{42}H_{22}N_2O_4$.)

This powerful alkaloid crystallizes in white lustrous prisms, or in octohedra. Cold water does not dissolve more than $\frac{1}{7000}$ of its weight, but nevertheless acquires a distinctly bitter taste; in ether and in absolute alcohol strychnia is insoluble, but in hot dilute alcohol it dissolves, crystallizing out on cooling. Its salts are soluble in alcohol. The *sulphate*, *nitrate*, and *hydrochlorate* dissolve in water, their solubility being much increased in the presence of free acid. Strychnia is insoluble in the caustic alkalies, but soluble in the essential oils and in chloroform.

Reactions with reagents.

Terchloride of gold gives a *reddish-yellow* precipitate.

Bichloride of platinum, a *yellow* granular precipitate.

Infusion of galls, a *white* precipitate.

Sulphocyanide of potassium, a white crystalline precipitate.

Nitric acid added to strychnia becomes *yellow*, if the acid be concentrated, it acquires at the first moment a *rose-red* tint, soon however becoming light-yellow.

Chlorine water gives a white precipitate soluble in ammonia.

Bichromate of potassa and *sulphuric acid* give rise to a beautiful *violet tint*, soon fading into a pale *rose-colour*. "If," observes Otto, "this experiment be executed with the necessary care, the strychnia deposited from one drop of an ethereal solution can be very distinctly recognized; but to obtain a distinct reaction it is requisite that the amount of bichromate be pro-

portional to the quantity of the alkaloid, and this is best attained by using the former in the shape of a solid piece, and neither as a powder nor in solution. After solution of the strychnia has been effected, the acid is spread out over the surface of a porcelain dish, and then the crystal of bichromate of potassa placed in it. On inclining the dish, *violet* stripes are noticed flowing from the salt, and on moving the crystal backward and forward by means of a glass rod, the whole of the liquid assumes a rich violet colour.

Other oxidizing agents produce a similar effect.

If a crystal of strychnia, or either of its salts, be placed on a slip of clean platinum-foil, and moistened with strong sulphuric acid, and if the foil be then connected with the *positive* pole of a small galvanic battery (two of Grove's cells are quite sufficient) and the wire from the *negative* pole be brought into momentary contact with the liquid (taking care that it does not touch the metal), the *violet* colour will instantly appear.

For the physiological test for strychnia, we are indebted to Dr. Marshall Hall. This consists in throwing fresh young frogs into tetanic convulsions by the action of the poison. The back of the animal should be cleaned with blotting-paper, previous to placing them in the liquid to be tested. Dr. Hall states that by this method $\frac{1}{5000}$ of a grain of strychnia may be detected, and Dr. Harley found that when a solution containing only $\frac{1}{16000}$ of a grain of acetate of strychnia was injected into the lungs of a very small frog, the animal became violently tetanic in nine and a half minutes, and died in two hours.

The best solvent for strychnia in complicated organic fluids is chloroform; the liquid having been previously made alkaline; on expelling the chloroform by gentle evaporation, the alkaloid remains behind, and may then be dissolved in dilute hydrochloric acid, and subjected to the above tests.

Animal charcoal possesses the property of removing alkaloids from solutions; it should never therefore be used as a decolorizing agent. Hofmann and Graham dissolved half a grain of strychnia in half a gallon of beer, and left two ounces of animal charcoal in contact with the liquid for twenty-four hours; the charcoal was then separated by filtration and boiled for half an hour with eight ounces of alcohol, fresh portions being added from time to time to replace the loss by evaporation. The alcohol was then removed by distillation, the residue mixed with caustic potassa, agitated with ether, and the ethereal solution allowed

to evaporate spontaneously in a watch glass. On the addition of a drop of sulphuric acid, and a particle of bichromate of potassa, the characteristic violet colour was produced.

128. Brucia. ($C_{46}H_{26}N_2O_8$,8aq.)

This alkaloid is more soluble in water than strychnia; it is soluble also in strong alcohol, by which it may be separated from strychnia; it crystallizes in small oblique rhombic prisms which are insoluble in ether; its taste is intensely bitter; it is less poisonous than strychnia; its salts are more soluble in water than those of strychnia.

Reactions with reagents.

Nitric acid produces a *bright red* colour, which soon becomes *yellowish-red*, and finally *yellow;* the addition of *protochloride of tin* changes the colour to *violet.*

Concentrated sulphuric acid produces a *rose-red* colour, which soon vanishes.

On adding *sulphuric acid* and *bichromate of potash* to a solution containing brucia, the *blue*, *violet*, and *purple* colours observed in strychnia are *not* produced.

129. Aconitina.

This intensely poisonous alkaloid generally occurs in whitish granular masses, without any distinct crystalline structure; it is sparingly soluble in water, more soluble in ether, and readily dissolved by alcohol. Its solution has a strong alkaline reaction, and it forms, with acids, salts which do not crystallize.

There are no reliable chemical tests whereby to identify this alkaloid, but Dr. Headland has recommended ('Lancet,' March 29th, 1856) as a physiological test, the application of a spirituous extract of the acid contents of the stomach. If $\frac{1}{20}$ of a grain be obtained it will be sufficient. He states that $\frac{1}{360}$ of a grain will poison a mouse with characteristic symptoms; $\frac{1}{100}$ a small bird; $\frac{1}{1000}$ of a grain causes tingling and numbness of the tip of the tongue; $\frac{1}{100}$ of a grain dissolved in spirit, and rubbed into the skin, causes loss of feeling lasting for some time.

130. Atropia. ($C_{34}H_{23}NO_6$.)

It occurs in white, silky needles, or as a vitreous mass. It is sparingly soluble in water, more so in ether, and dissolving

freely in alcohol and in chloroform. Its salts, which are easily soluble in water, are very unstable, suffering gradual decomposition by exposure to the air. Like *aconitina*, its reactions with reagents show nothing characteristic, but if a few drops of a solution of one part of sulphate of atropia in 9600 parts of water, be introduced into the eye, considerable dilatation of the pupil is produced, lasting from half an hour to an hour.

131. *Detection of the Poisonous Alkaloids in Organic Mixtures.*

The following process, recommended by Stas, has met with the approval of most toxicologists. It is founded on the observation, that the alkaloids form acid salts, which are soluble in water, and in alcohol, and that on decomposing a solution of this kind by means of an alkali, and agitating it with a sufficient quantity of ether, the liberated base dissolves in the ether. If the contents of a stomach, food, etc., are to be examined, they are mixed with double their weight of the strongest alcohol, from 10 to 30 grains of *tartaric* or *oxalic* acid are added, and the mass heated in a retort or flask to about 170° Fahr. Organs, such as liver, lungs, etc., must be cut into small shreds, moistened with alcohol and acid, then pressed, and this operation several times repeated. When cold, the liquid is strained through filtering-paper, and the residue washed with strong alcohol. The filtrate is evaporated, nearly to dryness, at a temperature not exceeding 100° Fahr., in a current of air, or still better in vacuo over sulphuric acid. The residue is exhausted with cold anhydrous alcohol; the extract is evaporated; the residue is dissolved in the smallest possible quantity of water, and the solution saturated with bicarbonate of soda. The liquid is then agitated with from four to six times its volume of pure, rectified ether; the alkaloid will be found in the ethereal solution. A small portion is tested for the volatile alkaloids (*nicotine*, *conia*,) by allowing it to evaporate spontaneously in a watch-glass.

132. (1) *A Volatile Alkaloid is indicated.*

In this case the whole ethereal solution is agitated with a strong solution of caustic potassa, and allowed to stand; the ether which has collected on the surface is then poured off, and agitated with pure dilute sulphuric acid, and allowed to remain at rest for some time; the volatile alkaloids are hereby converted into sulphates and are contained in the *aqueous* solution;

this is now to be agitated with caustic soda or potassa and again treated with ether. The ethereal solution contains the alkaloid now in a pure state as regards animal matters, but containing perhaps ammonia, from which it is freed by spontaneous evaporation, or *in vacuo* over sulphuric acid; the ammonia being expelled, the residue is in a state to be chemically examined.

133. (2) *A Fixed Alkaloid is indicated.*

The solution, after saturation with bicarbonate of soda, is completely extracted by repeated agitation with pure rectified ether, and the ethereal solution exposed to spontaneous evaporation. The residue, which is distinctly alkaline and contains much animal matter, is dissolved in a small quantity of dilute alcohol, and allowed spontaneously to evaporate; the residue is treated with dilute sulphuric acid and allowed to stand; the clear liquid is concentrated in vacuo over sulphuric acid, a very concentrated solution of carbonate of potassa is added, and then anhydrous alcohol; the alcoholic solution on evaporation yields the alkaloid in crystals the nature of which is examined.

By this process, Stas has succeeded in isolating from mixtures with foreign substances, *morphia*, *codeia*, *strychnia*, *brucia*, *veratria*, *aconitina*, *atropia*, and several other alkaloids. When the presence of *opium* has to be established, the suspected matters are treated with dilute alcohol and a little hydrochloric acid, the extract is concentrated by evaporation, the residue dissolved in water, filtered, and the filtrate mixed with *magnesia* in excess, heated to ebullition and then again filtered. The resulting liquid contains *meconate of magnesia*, which, when acidulated with hydrochloric acid, strikes the characteristic *blood-red* colour with sesquichloride of iron; but as some kinds of opium do not contain meconic acid, it may be advisable to treat the suspected substance for *morphia* in the manner above described.

CHAPTER VI.

ON SYSTEMATIC QUALITATIVE ANALYSIS.

184. In the Third Chapter the chemical comportment of a great number of substances with reagents has been described. Amongst the bases there have been omitted only a few metallic oxides of rare occurrence; and amongst the acids, nearly all in the inorganic, and a great number of those in the organic kingdom that are of anything like frequent occurrence, have been included. Now when the student has made himself *experimentally* acquainted with the relations of these substances to reagents, and when he has become familiar with all the leading reactions that have been described, he is in a position certainly to pronounce a correct opinion as to the nature of almost any arrangement of a *single base* with a *single acid* (or element replacing it), that may be presented to his notice; but if he be called upon to decide upon the nature of a compound, consisting perhaps of a mixture of several substances, it is clear that a mere knowledge of the action of reagents *alone*, will not serve him, but that he must possess the knowledge also of a method of *separating* the various substances from each other, and of determining the *absence* or *presence* of certain bases and acids: in short, he must know how to proceed on a *systematic method* of examination, without which chemical analysis would be little better than mere guess-work, and its *correctness* or *incorrectness* quite a matter of chance. Even in the examination of a compound which is known to consist of a single acid and a single base only, the greatest advantage is derived from the systematic method, a great saving of time and labour is effected, and the result is arrived at in a far more satisfactory manner than it could be by the indiscriminate application of test after test, following no rule or order, but

merely throwing out baits, as it were, with the hope of eventually meeting with appearances, and of observing phenomena, that may enable us to recognize the presence of some particular substance. In this Chapter our object will be to point out the manner in which this systematic method of qualitative analysis is to be conducted; and our attention will be confined to those substances and combinations only which are of *general* occurrence. The subject will be thus rendered far more inviting, and less embarrassing, to the beginner; and, after the student has made himself thoroughly acquainted with the *principles* on which general examinations are conducted, and has acquired a dexterity in conducting the manipulatory processes, he will afterwards find no difficulty in encountering the analysis of compounds in which the rarer substances occur, to the existence of which a careful preliminary examination will, generally speaking, arouse his attention.

PRELIMINARY EXAMINATION.

135. Before submitting a compound to analysis in the *wet* way, there are certain *dry* operations to be performed upon it which should never be neglected, as they frequently furnish valuable hints for the subsequent examination, and always give some insight into the nature of the substance; though it must particularly be borne in mind that the absence of many of the reactions about to be described does not *necessarily* imply the *absence* of particular bodies, since when several substances are present together, one reaction frequently masks or altogether destroys another. Nevertheless, although the wet analysis of a compound will almost invariably be necessary, the preliminary dry assay is not without its value, as it draws special attention to the presence of various bodies, when the operator is performing the systematic analysis.

136. In the first place, the physical characters of the substance are noted, such as its *form*, *density*, *colour*, *hardness*, etc. It should then be reduced to powder, and subjected to the action of heat, both alone, and also together with certain fluxes. The experiments are conducted in the following manner:—

I. A small portion of the substance reduced to a state of fine division, is introduced into a tube of hard glass open at both ends, and about one-third of an inch in diameter, and heated in the flame of a gas or spirit lamp.

A. It does not change.

No *organic matter* is present; the absence of *hydrates;* of salts containing *water* of *crystallization;* of readily *fusible* substances, and of *volatile* substances, is also indicated.

B. It changes colour.

(1) It is *yellow* while hot, but becomes *white* on cooling. *Oxide of zinc* is probably present.

(2) When hot it assumes a *yellowish-brown* colour, and on cooling a permanent *dirty yellow. Binoxide of tin* is probably present.

(3) While hot the colour is *reddish-brown;* the colour becomes *yellow* on cooling. *Oxide of lead* is probably present.

(4) When hot *deep-yellow; dull-yellow* on cooling. *Oxide of bismuth* is probably present.

C. It emits gases or fumes, or intumesces.

(1) A splinter of wood, red-hot at the end, burns vividly when introduced into the upper end of the tube (O). *Peroxides, chlorates, nitrates, iodates,* and *bromates* either, or all, may be expected to be present.

(2) A smell like that of a burning sulphur-match is recognized; the evolved vapour bleaches litmus-paper. The presence of one of the lower oxides of *sulphur* is indicated.

(3) Vapours of a reddish-brown colour are emitted. The presence of *nitrates* (especially those of the heavy metals) is indicated.

(4) A gas is disengaged which extinguishes the flame of a burning body, and which, when passed into *lime* water or *baryta* water causes turbidity. The presence of *carbonic acid* is indicated.

(5) A gas is disengaged which burns with a blue flame (CO), the substance not necessarily changing colour. The presence of *oxalic acid* is indicated; that acid, and the oxalates, decomposing into CO and CO_2 by heat.

(6) An inflammable gas, burning with a peach-coloured flame, and emitting the peculiar smell of oil of bitter almonds, is evolved. Some *cyanogen* compounds are present.

(7) A gas emitting a strong odour of rotten eggs is evolved; a piece of paper moistened with a solution of a lead salt is *blackened* when introduced into the gas. *Hydrosulphuric acid*

(*sulphuretted hydrogen*), arising probably from *moist* sulphides, is indicated.

(8) A pungent gas is evolved which restores the blue colour of reddened litmus-paper, and causes dense fumes when a glass rod moistened with strong acetic acid is brought into contact with it. *Ammonia* is indicated, which may arise from the decomposition of ammoniacal salts, from the decomposition of nitrogenous organic matters, or possibly from the decomposition of some cyanogen compounds.

(9) A vapour rises from the heated substance which condenses in the cooler parts of the tube.

a. The condensed liquid does not affect the colour of litmus-paper: *it is pure water*. Some salt or salts containing water of crystallization, (*alums, borates, alkaline phosphates*, etc.,) are present.

β. The condensed liquid has an *alkaline* reaction. *Ammonium* compounds are indicated.

γ. The condensed liquid has an *acid* reaction. Some volatile acid is indicated (*sulphuric, sulphurous, hydrofluoric, hydrochloric, hydrobromic, hydriodic, nitric*, etc.).

(10) The substance *sublimes with*, or *without odour*, and is deposited on the cold sides of the tube. Various volatile salts may be present, also *arsenious acid, benzoic acid*, etc.; also *sulphur* (condensing in brown oily drops.)

II. A small portion of the substance is heated in a closed tube with carbonate of soda.

A. It does not blacken.

(1) A *metallic mirror* is formed on the cooler part of the tube, which cannot be resolved into metallic globules by rubbing it with a glass rod, and which, on further heating, is volatilized, and again sublimed in the form of octahedral crystals. *Arsenical compounds* are indicated.

(2) A *metallic mirror* is formed, resolvable into metallic globules by rubbing with a glass rod. *Mercurial compounds* are indicated.

(3) No metallic sublimate, but an aromatic odour of frankincense emitted. A salt of *benzoic* acid probably present.

(4) No metallic sublimate, but powerfully irritating fumes. *Succinic acid* is probably present.

B. It blackens.

(1) A peculiar odour (acetone) is evolved. Presence of *acetates*.

(2) A colourless residue, soluble with effervescence in hydrochloric acid. One or more of the *organic acids* in combination with alkalies or alkaline earths may be present.

III. A small portion of the substance is heated on charcoal in the *inner* blowpipe flame.

(1) The substance *colours the outer flame*—

- α. *Golden yellow*, indicating *sodium*.
- β. *Violet*, indicating *potassium*.
- γ. *Yellowish-green*, indicating *barium*.
- δ. *Crimson*, indicating *strontium*.
- ε. *Reddish-yellow*, indicating *calcium*.
- ζ. *Green*, indicating *copper*, *phosphoric acid*, *boracic acid*.
- η. *Blue*, indicating *antimony*, *lead*, *arsenious acid*, *chloride of copper*.

(2) The substance *deflagrates*, indicating *nitrates*, or *chlorates*.
The substance *decrepitates*, indicating *chloride of sodium*.
The substance *intumesces*, indicating *alums*, *borates*.

(3) The substance *fuses readily* and is *absorbed by the charcoal*, indicating *alkaline salts*.

(4) The substance does not fuse, but *leaves a white residue*. Salts of *barium*, *strontium*, *calcium*, *magnesium*, *aluminum*, *zinc*, and *silicic acid* may be present; if it become highly luminous on ignition, oxides of *strontium*, *calcium*, *magnesium*, and *zinc* must be looked for. If on moistening the cold residue with nitrate of cobalt and again strongly igniting, it assume a fine *blue* colour, *alumina*, or *earthy phosphates*, are present; if it become *pale-red*, *magnesia*; if *green*, *oxide of zinc*.

(5) The substance does not fuse, but *leaves a coloured residue*. Heat a small fragment on a clear borax bead on platinum wire, in the *outer* flame of the blowpipe.

- α. The bead is *blue* when hot, and *blue* when cold. Characteristic of *oxide of cobalt*.
- β. The bead is *green* when hot, and *blue* when cold. Characteristic of *oxide of copper*.
- γ. The bead is *green* when hot, and *green* when cold. Characteristic of *sesquioxide of chromium*.
- δ. The bead is *brownish-red* when *hot*, and *orange* when cold. Characteristic of *sesquioxide of iron*.

ε. The bead is *reddish-brown*, becoming lighter on cooling. Characteristic of *oxide of nickel.*

ζ. The bead is *yellowish-brown* while hot, the colour becoming very faint on cooling. Characteristic of *oxide of bismuth.*

η. The bead is *amethyst colour* while hot, becoming lighter or altogether vanishing on cooling. Characteristic of *oxide of manganese.*

IV. A little of the substance is mixed with carbonate of soda, or with a mixture of carbonate of soda and cyanide of potassium, and heated in the inner blowpipe flame.

(1) The substance is *reduced to the metallic state without incrustation.*

α. The metal appears in white shining scales. *Silver; tin.*

β. The reduced metal is red. *Copper.*

γ. The reduced metal is *yellow. Gold.*

(2) The substance is *reduced to the metallic state with incrustation.*

α. The reduced metal is brittle, the incrustation is *white. Antimony.*

β. The reduced metal is brittle, the incrustation is *brown-yellow. Bismuth.*

γ. The reduced metal is *not* brittle, the incrustation is *yellow. Lead.*

(3) The substance is *not reduced to the metallic state, but it furnishes an incrustation.*

α. The incrustation is *white. Oxide of zinc.*

β. The incrustation is *brownish-red. Oxide of cadmium.*

γ. The incrustation is *white*, and garlic-smelling fumes are emitted. Compounds of *arsenic.*

(4) An alkaline sulphide is left which stains metallic silver black. Compounds of *sulphur.*

137. If the substance to be analysed be a liquid, the first step is to evaporate a portion of it to dryness on platinum foil, in order to see whether it really contain anything in solution, and then to ascertain, by means of test-papers, whether it has an acid, or alkaline, or neutral reaction; if the first, it does not necessarily follow that the solution contains free acid, for it must be borne in mind that saline

solutions of many of the heavy metallic oxides redden litmus-paper. It is not difficult, however, to decide whether the acid reaction is occasioned by a metallic salt or by a free acid; the addition of a drop or two of solution of carbonate of potassa or soda generally, in the first case, renders the liquid turbid; while, in the latter case, it remains clear. If the solution be *alkaline*, it can contain no metallic oxides that are insoluble in alkaline liquids; and if it be perfectly neutral, it probably consists only of salts of the alkalies, or alkaline earths.

138. These preliminary experiments having been made, and some insight into the general nature of the substance under examination having thereby been obtained, its relation to *solvents* is next to be examined. It is reduced to a fine state of division by trituration in an agate mortar, and a portion digested for some time in a test-tube with distilled water; if it be entirely dissolved, the qualitative analysis of the aqueous solution may at once be proceeded with, taking about twenty-five or thirty grains of the substance. If a complete solution do not take place, a drop or two of the clear liquid is to be evaporated to dryness on platinum foil, in order to see whether water has dissolved anything. If the evaporated liquid leave a residue, then the substance must a second, and a third time, be digested with fresh portions of distilled water, filtered, and the filtrate set aside for subsequent examination. The undissolved residue is next gradually heated to boiling, with *dilute* hydrochloric acid, and if complete solution be not effected, the fluid is decanted, and the residue digested with *concentrated* hydrochloric acid, particular attention being paid to the nature of the gases evolved. If an effervescence take place, *carbonic acid*, *sulphuretted hydrogen*, and *hydrogen* gases may be looked for; the first betrays the presence of *carbonates*, the second that of *sulphides*, the third that of certain *metals*; the evolution of *chlorine* indicates *peroxides* or *chromates*, and *hydrocyanic acid* points out the existence of certain *cyanides*. If complete solution of the substance be not effected by concentrated hydrochloric acid, a fresh portion is to be digested with nitric acid; a few of the metals only, escape solution by this acid (*gold*, *platinum*, *palladium*, etc.); *tin* and *antimony* are oxidized by it, but the oxides are not dissolved; it moreover decomposes all sulphides, with the single exception of *sulphide of mercury*, setting free *sulphur*, which is easily recognized by its colour and lightness, and its being completely evaporated when heated

on a strip of platinum foil. If nitric acid fail to dissolve the substance completely, *aqua-regia* may be tried, and if this leave a residue, recourse must be had to fusion with an alkali or an alkaline carbonate, the following preliminary experiments being first performed upon it.

(1) A small portion is heated on a slip of platinum foil; the odour of sulphurous acid is conclusive as to the presence of *sulphur*, and, if no other substance be present, the whole will be dissipated by a very moderate heat; in this case, a prolonged digestion of the residue in *aqua-regia* will, generally speaking, give a clear solution, the whole of the sulphur becoming oxidized into sulphuric acid.

(2) A small quantity is moistened with *sulphide of ammonium;* if it immediately become black, an insoluble *silver, mercury*, or *lead* salt is present.

(3) A small portion is mixed with carbonate of soda, and heated in the inner blowpipe flame; a metallic reduction, accompanied by a yellow incrustation, indicates *lead.*

(4) A small quantity is digested with carbonate of potassa or soda; if it become black, *subchloride of mercury* is present, which is further confirmed by mixing a portion of the residue with slightly moistened carbonate of soda, and heating it in a glass tube; small globules of mercury are easily recognized with the aid of a lens.

(5) Another small quantity may be digested with ammonia, and the clear ammoniacal liquid supersaturated with nitric acid; the formation of a white precipitate, insoluble in the nitric acid, indicates *silver.*

Besides insoluble compounds of *silver, lead,* and *mercury*, the residue insoluble in aqua-regia, may contain *sulphates of the alkaline earths, silicates, fluorides, certain phosphates and arseniates, and the insoluble modifications of oxides of tin, antimony,* and *chromium. Sesquioxide of iron* also is dissolved only with great difficulty, after having been strongly ignited. All these compounds may, however, be brought into a soluble state by fusion with carbonate of soda, or better with a mixture of carbonate of soda and carbonate of potassa, or of carbonate of soda and cyanide of potassium, their constituents being thereby transposed in such a manner as to admit of their easy detection by a proper subsequent treatment. For example, if the original substance undissolved by nitric acid, or by aqua-regia, contain sulphates of the alkaline earths, the result of a fusion with

carbonate of soda is to bring them to the state of carbonates, which, though insoluble in water, are readily dissolved by dilute hydrochloric acid, and the bases are then easily detected in the hydrochloric solution: the sulphuric acid with which these bases were previously combined, is found in the *aqueous* solution of the fused mass, in the form of *sulphate of soda*. Again, if the insoluble residue contain *chloride*, *iodide*, or *bromide of silver* or *lead*, the result of the fusion with an alkaline carbonate, which in this case must be performed in a porcelain, and not in a platinum crucible, is to transfer the *chlorine*, *bromine*, or *iodine* to the metal of the alkaline base, forming compounds easily soluble in water, and therefore easy of detection in the aqueous solution of the fused mass; while the *metal* or *metals* with which the chlorine, iodine, or bromine was originally combined, being of course insoluble in water, may be dissolved in nitric acid, and detected by the appropriate tests. If *baryta*, *strontia*, and *lime* be present, besides the oxides of *silver* and *lead*, the two latter metals are precipitated from the nitric solution by sulphuretted hydrogen: the liquor filtered from the precipitate, is nearly neutralized with carbonate of soda, and mixed with hydrofluosilicic acid, by which the *baryta*, after a time, is precipitated. To the liquor filtered from this precipitate, solution of sulphate of potassa is added, which precipitates the *strontia* in company, perhaps, with a little of the lime, and on filtering off the precipitated sulphate of strontia, adding to the filtrate ammonia, and then oxalate of ammonia, a white precipitate, indicating the presence of *lime*, is determined. *Silicic acid*, if present, passes into the state of silicate of soda, and is discovered by adding excess of hydrochloric acid to the aqueous solution of the fused mass, evaporating to perfect dryness, and treating the residue with water; by this treatment the silicic acid is brought to its insoluble condition, and remains undissolved.

139. It thus appears that when we have before us a complex substance, which is partly soluble in water, and not wholly dissolved by either hydrochloric acid, nitric acid, or aqua-regia, three distinct analytical operations may be performed on it, viz.: —1. *An analysis* of the aqueous solution. 2. *An analysis* of the acid solution. 3. *An analysis* of the insoluble residue. If the operator be desirous of obtaining a precise knowledge of the mode of arrangement of the different acids and bases in such a complex mixture, he must make these three distinct analyses; but, if his object be only to ascertain what acids and

bases are present, he may generally omit a distinct analysis of the aqueous solution, and after a careful preliminary examination, he may confine his attention to the acid solution (the substance not having been previously exhausted by water), and to the mass obtained by fusion of the residue with an alkali.

I.—Examination for Bases: principles upon which the method depends.

140. In the Third Chapter, it was shown that by means of certain *general* reagents, metals may be arranged into *groups;* some of which, by other reagents, may again be subdivided into *minor* groups, each of the individuals composing which may be recognized by their comportment with certain other reagents, which may be called *special.*

141. The general reagents are *hydrochloric acid, hydrosulphuric acid (sulphuretted hydrogen), sulphide of ammonium, ammonia,* and the *carbonates of soda, ammonia,* and *potassa;* they are of the greatest use to the analytical chemist in conducting a systematic qualitative analysis. Thus, if on the addition of hydrochloric acid to a solution, no precipitate or turbidity should occur, the operator is assured that no salt of *silver* or of *suboxide of mercury* is present; neither can the liquid contain any considerable quantity of a salt of *lead;* again, if on the addition of sulphuretted hydrogen water in excess, no alteration should be perceptible, no member of the *fifth group* can be present; and if, after having neutralized the liquid with ammonia, no precipitate, or decided change of colour should occur, on the addition of sulphide of ammonium, even on the application of heat, absence of all members of the *fourth group* is indicated, and the solution can contain no bases but some one or more of the *first* or *second* groups; and lastly, the addition of an alkaline carbonate will show at once, whether any of the alkaline earths are present. If this reagent should give no precipitate, then the solution in question can contain no metallic oxides but *magnesia,* and those contained in the *first group;* and if *phosphate of soda* should occasion no precipitate or turbidity, even after agitation and standing, it must be a solution of some salt, or salts, of one or more of the alkalies proper.

142. Let us assume, however, that the reagents have given indications of the presence of some one or more of the members of *all* the groups; the solution must then be submitted to a careful analysis, in accordance with the following scheme.

A. *Hydrochloric acid has produced a precipitate, which does not disappear when the acid is added in excess, and the solution warmed.*

The precipitate must be *chloride of* SILVER, *chloride of* LEAD, *subchloride of* MERCURY, either or all, *possibly* also *benzoic acid* and *uric acid;* and if the acid has not been added in sufficient quantity and the solution warmed, *oxychlorides of* BISMUTH, ANTIMONY, and TIN; but as the absence of all these bodies is secured by heating the well-acidified solution, regard need only be had to SILVER, MERCURY, and LEAD.

Analysis of the Precipitate by Hydrochloric Acid.

It is thrown on a filter and washed thoroughly with boiling water.

(1) The washings may contain *chloride of* LEAD, which, if present in quantity, crystallizes out as the solution cools in white needles.

Confirmation.—Sulphuric acid produces a *white* precipitate; bichromate of potassa produces a *yellow* precipitate.

LEAD is present.

(2) The insoluble portion on the filter may be *chloride of* SILVER and *subchloride of* MERCURY; wash the precipitate from the filter with ammonia, add that reagent in excess, and allow the insoluble portion (if any) to subside. The solution may contain *chloride* of SILVER.

Confirmation.—*Dilute nitric acid* added in excess produces a white curdy precipitate.

SILVER is present.

The insoluble *black* residue is *subchloride of mercury.*

Confirmation.—Dry at a gentle heat; mix with *dry* carbonate of soda, and heat the mixture in a bulb tube of hard glass; *metallic globules* are deposited in the upper part of the tube.

MERCURY is present.

B. *Hydrosulphuric acid water (sulphuretted hydrogen) produces with the filtrate from the precipitate by hydrochloric acid* (A) *a coloured precipitate; thoroughly saturate the solution with hydrosulphuric acid gas.*

The precipitate may contain *sulphides* of MERCURY, LEAD, BISMUTH, COPPER, CADMIUM, TIN, ARSENIC, ANTIMONY (GOLD and PLATINUM); the last two metals are to be tested for *specially,* in a portion of the original solution.

Throw on a filter; wash the precipitate until it is quite

free from hydrochloric acid; transfer the precipitate to a flask, boil it for some time with solution of *caustic potassa*, and filter.

(1) Analysis of the portion of the precipitate by Hydrosulphuric Acid soluble in Caustic Potash.

It may contain ANTIMONY, ARSENIC, and TIN.

Add hydrochloric acid in excess, and thoroughly saturate with hydrosulphuric acid. The above metals are re-precipitated as *sulphides*. Filter and wash. Dissolve in as little aqua-regia as possible, and introduce the solution into a gas-evolution bottle, together with a slip of zinc, and some dilute sulphuric acid, (both free from arsenic) gas is evolved, which is washed by passing through a second bottle containing a dilute solution of *acetate of lead*, and is conducted into a precipitate glass containing a solution of *nitrate of silver*. If a precipitate occur, allow the gas to pass until no further effect is produced.

This precipitate may contain ANTIMONY: collect it on a filter, wash thoroughly, and then boil it with tartaric acid; filter, acidify the filtrate with hydrochloric acid, and saturate with hydrosulphuric acid.

An *orange-coloured* precipitate is produced.

ANTIMONY is present.

The filtrate from the precipitate formed in the nitrate of silver may contain ARSENIC. Add a few drops of acetate of potassa.

A *light-yellow* precipitate is formed (arsenite of silver).

ARSENIC is present.

If any TIN be present it will have been precipitated on the slip of zinc in the gas-evolution bottle, in the form of a black powder, which is easily removed from the zinc. It should be dissolved in a small quantity of strong hydrochloric acid, diluted with water and mixed with a little solution of *chloride of mercury*.

A grey precipitate is formed (metallic mercury).

TIN is present.

(2) Analysis of the portion of the precipitate by Hydrosulphuric Acid insoluble in Caustic Potash.

It may contain MERCURY, LEAD, BISMUTH, COPPER, and CADMIUM.

Thoroughly wash; then boil with strong *nitric acid* as long as red fumes are evolved; add *dilute sulphuric* acid as long as a precipitate continues to form. If this precipitate be white, it contains probably *sulphate of lead;* if black, it contains *sul-*

phide of mercury; if pale-yellow and flocculent, it is probably only *sulphur*. Filter, wash, and digest with *acetate of ammonia*, and filter; add to the filtrate acetic acid in excess, and then solution of chromate of potash.

A *yellow* precipitate is formed.

LEAD is present.

The residue insoluble in acetate of ammonia (if black) is *sulphide of* MERCURY.

Confirmation.—Dry at a temperature not above that of boiling water, mix with dry carbonate of soda, and heat in bulb tube of hard glass. *Metallic globules* are deposited in the upper part of the tube.

MERCURY is present.

The portion soluble in nitric acid may contain COPPER, CADMIUM, and BISMUTH.

Digest with excess of *ammonia*, and filter.

The solution may contain CADMIUM and COPPER; add *hydrochloric acid* in excess, and then saturate with *hydrosulphuric acid*. Filter; wash with hydrosulphuric acid water; boil with *dilute sulphuric acid*, and filter rapidly.

The filtrate may contain CADMIUM. Thoroughly saturate with *hydrosulphuric acid*.

A yellow precipitate is formed.

CADMIUM is present.

The residue on the filter (if any) is *sulphide of* COPPER. Dissolve in *nitric acid* and add excess of *ammonia*: a *blue* solution is formed.

Confirmation.—Add *acetic acid*, and then *ferrocyanide of potassium*: a *chocolate*-coloured precipitate is produced.

COPPER is present.

If ammonia has failed to redissolve the whole of the portion insoluble in caustic potash, but soluble in nitric acid, the insoluble portion is probably BISMUTH.

Confirmation.—Redissolve in dilute *nitric* acid, add a few drops of *hydrochloric* acid, evaporate nearly to dryness, and then add a large quantity of water: the liquid becomes *milky*.

BISMUTH is present.

C. *Analysis of the filtrate from the precipitate occasioned by hydrosulphuric acid.*

It may contain all the metals of the *first*, *second*, *third*, and

fourth groups, likewise *phosphoric acid* in combination with *sesquioxides of iron, chromium*, and *aluminum*, and with *baryta, strontia, lime*, and *magnesia*.

Evaporate till the smell of sulphuretted hydrogen has disappeared; add a few drops of concentrated *nitric acid*, and continue the evaporation to perfect dryness. Should organic matter, or any of the organic acids have been indicated in the preliminary examination, the dry residue must be heated to redness to destroy them, since their presence in the solution to be analysed would prevent the precipitation of iron and alumina, but in the absence of organic matter, ignition of the residue may be dispensed with; in any case, it should not be heated too strongly, as certain oxides (*sesquioxide of iron* and *sesquioxide of chromium*) are dissolved with difficulty after having been ignited. Warm the dry, or the ignited residue with concentrated *hydrochloric acid*, then add water, and heat until it is entirely redissolved, or at any rate until no further action takes place. Should a *white* residue be left, it is probably *silicic acid, possibly sulphates of baryta* and *strontia*; should the residue be coloured, it probably contains *sesquioxide of iron* or *sesquioxide of chromium*. A little experience will enable the operator to decide whether the insoluble residue requires further examination; should he deem such to be necessary, he must proceed with it according to the instructions given under E. Filter from the insoluble residue (if any), add abundance of *chloride of ammonium*, then *ammonia* in excess, warm gently, and filter *rapidly*.

I. Analysis of the portion precipitated by Ammonia.

It may contain *sesquioxides* of IRON, CHROMIUM, and ALUMINUM, also the *phosphates* of those *sesquioxides*: it may also contain the *phosphates* of BARYTA, STRONTIA, LIME, and MAGNESIA. The further treatment of the precipitate depends upon the presence or absence of *phosphoric acid*. Dissolve a small portion in hydrochloric acid, and test with *molybdate of ammonia*.

a. Phosphoric Acid is present.

Boil the rest of the precipitate with *oxalic acid;* when cold, add *acetate of potash*, shake well, allow to stand for some time, and then filter.

The insoluble portion may contain BARYTA, STRONTIA, and LIME, now in combination with *oxalic acid*. It is collected upon a filter, well washed, and then dried and ignited, by

B. It blackens.

(1) A peculiar odour (acetone) is evolved. Presence of *acetates*.

(2) A colourless residue, soluble with effervescence in hydrochloric acid. One or more of the *organic acids* in combination with alkalies or alkaline earths may be present.

III. A small portion of the substance is heated on charcoal in the *inner* blowpipe flame.

(1) The substance *colours the outer flame*—

- α. *Golden yellow*, indicating *sodium*.
- β. *Violet*, indicating *potassium*.
- γ. *Yellowish-green*, indicating *barium*.
- δ. *Crimson*, indicating *strontium*.
- ε. *Reddish-yellow*, indicating *calcium*.
- ζ. *Green*, indicating *copper*, *phosphoric acid*, *boracic acid*.
- η. *Blue*, indicating *antimony*, *lead*, *arsenious acid*, *chloride of copper*.

(2) The substance *deflagrates*, indicating *nitrates*, or *chlorates*.
The substance *decrepitates*, indicating *chloride of sodium*.
The substance *intumesces*, indicating *alums*, *borates*.

(3) The substance *fuses readily* and is *absorbed by the charcoal*, indicating *alkaline salts*.

(4) The substance does not fuse, but *leaves a white residue*. Salts of *barium*, *strontium*, *calcium*, *magnesium*, *aluminum*, *zinc*, and *silicic acid* may be present; if it become highly luminous on ignition, oxides of *strontium*, *calcium*, *magnesium*, and *zinc* must be looked for. If on moistening the cold residue with nitrate of cobalt and again strongly igniting, it assume a fine *blue* colour, *alumina*, or *earthy phosphates*, are present; if it become *pale-red*, *magnesia*; if *green*, *oxide of zinc*.

(5) The substance does not fuse, but *leaves a coloured residue*. Heat a small fragment on a clear borax bead on platinum wire, in the *outer* flame of the blowpipe.

- α. The bead is *blue* when hot, and *blue* when cold. Characteristic of *oxide of cobalt*.
- β. The bead is *green* when hot, and *blue* when cold. Characteristic of *oxide of copper*.
- γ. The bead is *green* when hot, and *green* when cold. Characteristic of *sesquioxide of chromium*.
- δ. The bead is *brownish-red* when *hot*, and *orange* when cold. Characteristic of *sesquioxide of iron*.

(*sulphuretted hydrogen*), arising probably from *moist* sulphides, is indicated.

(8) A pungent gas is evolved which restores the blue colour of reddened litmus-paper, and causes dense fumes when a glass rod moistened with strong acetic acid is brought into contact with it. *Ammonia* is indicated, which may arise from the decomposition of ammoniacal salts, from the decomposition of nitrogenous organic matters, or possibly from the decomposition of some cyanogen compounds.

(9) A vapour rises from the heated substance which condenses in the cooler parts of the tube.

- α. The condensed liquid does not affect the colour of litmus-paper: *it is pure water*. Some salt or salts containing water of crystallization, (*alums*, *borates*, *alkaline phosphates*, etc.,) are present.
- β. The condensed liquid has an *alkaline* reaction. *Ammonium* compounds are indicated.
- γ. The condensed liquid has an *acid* reaction. Some volatile acid is indicated (*sulphuric*, *sulphurous*, *hydrofluoric*, *hydrochloric*, *hydrobromic*, *hydriodic*, *nitric*, etc.).

(10) The substance *sublimes with*, or *without odour*, and is deposited on the cold sides of the tube. Various volatile salts may be present, also *arsenious acid*, *benzoic acid*, etc.; also *sulphur* (condensing in brown oily drops.)

II. A small portion of the substance is heated in a closed tube with carbonate of soda.

A. It does not blacken.

(1) A *metallic mirror* is formed on the cooler part of the tube, which cannot be resolved into metallic globules by rubbing it with a glass rod, and which, on further heating, is volatilized, and again sublimed in the form of octahedral crystals. *Arsenical compounds* are indicated.

(2) A *metallic mirror* is formed, resolvable into metallic globules by rubbing with a glass rod. *Mercurial compounds* are indicated.

(3) No metallic sublimate, but an aromatic odour of frankincense emitted. A salt of *benzoic* acid probably present.

(4) No metallic sublimate, but powerfully irritating fumes. *Succinic acid* is probably present.

B. It blackens.

(1) A peculiar odour (acetone) is evolved. Presence of *acetates*.

(2) A colourless residue, soluble with effervescence in hydrochloric acid. One or more of the *organic acids* in combination with alkalies or alkaline earths may be present.

III. A small portion of the substance is heated on charcoal in the *inner* blowpipe flame.

(1) The substance *colours the outer flame*—

- α. *Golden yellow*, indicating *sodium*.
- β. *Violet*, indicating *potassium*.
- γ. *Yellowish-green*, indicating *barium*.
- δ. *Crimson*, indicating *strontium*.
- ε. *Reddish-yellow*, indicating *calcium*.
- ζ. *Green*, indicating *copper*, *phosphoric acid*, *boracic acid*.
- η. *Blue*, indicating *antimony*, *lead*, *arsenious acid*, *chloride of copper*.

(2) The substance *deflagrates*, indicating *nitrates*, or *chlorates*.
The substance *decrepitates*, indicating *chloride of sodium*.
The substance *intumesces*, indicating *alums*, *borates*.

(3) The substance *fuses readily* and is *absorbed by the charcoal*, indicating *alkaline salts*.

(4) The substance does not fuse, but *leaves a white residue*. Salts of *barium*, *strontium*, *calcium*, *magnesium*, *aluminum*, *zinc*, and *silicic acid* may be present; if it become highly luminous on ignition, oxides of *strontium*, *calcium*, *magnesium*, and *zinc* must be looked for. If on moistening the cold residue with nitrate of cobalt and again strongly igniting, it assume a fine *blue* colour, *alumina*, or *earthy phosphates*, are present; if it become *pale-red*, *magnesia*; if *green*, *oxide of zinc*.

(5) The substance does not fuse, but *leaves a coloured residue*. Heat a small fragment on a clear borax bead on platinum wire, in the *outer* flame of the blowpipe.

- α. The bead is *blue* when hot, and *blue* when cold. Characteristic of *oxide of cobalt*.
- β. The bead is *green* when hot, and *blue* when cold. Characteristic of *oxide of copper*.
- γ. The bead is *green* when hot, and *green* when cold. Characteristic of *sesquioxide of chromium*.
- δ. The bead is *brownish-red* when *hot*, and *orange* when cold. Characteristic of *sesquioxide of iron*.

one portion add *sulphate of lime.* A white precipitate is formed after a time.

STRONTIA is present.

Dilute the other part of the solution with water, add a drop of *ammonia* and *oxalate of ammonia.* A white precipitate is produced.

LIME is present.

II. Treatment of the Filtrate from the Precipitate by Carbonate of Ammonia.

It may contain MAGNESIA, and the ALKALIES. Add a few drops of *carbonate of ammonia*, to be assured that everything precipitable by that reagent has been removed. Should the solution remain clear, to a small portion add *ammonia* and *phosphate of soda*, and agitate. A white crystalline precipitate is formed.

MAGNESIA is present.

Evaporate the remainder of the solution to dryness, and ignite till ammoniacal fumes cease to be evolved. Heat a small portion of the ignited residue on platinum wire, in the *inner* flame of the blowpipe. The outer flame is tinged *yellow.*

SODA is present.

Redissolve the remainder of the ignited residue in a little hot water; add a drop of *hydrochloric acid*, and a few drops of *bichloride of platinum*, and stir. A *yellow* crystalline precipitate is formed.

POTASSA is present.

Ammonia, if present, will have been formed in the preliminary examination.

E. *Analysis of the portion insoluble in water and in acids.*

It may contain LEAD, BARYTA, STRONTIA, and LIME, as sulphates; LEAD and SILVER, as *chlorides;* it may also contain the insoluble modifications of the *sesquioxides* of ALUMINUM, IRON, and CHROMIUM; *silicates*, *aluminates*, and *fluorides;* and *binoxide of* TIN, and certain *phosphates*, *arseniates*, and *antimoniates*. A small portion is first submitted to a careful preliminary examination by the blowpipe, whereby a general knowledge of its nature is obtained. It is then fused with three or four times its weight of a mixture of *carbonate of potassa* and *carbonate of soda:* the fusion may be made in a platinum crucible, unless the preliminary examination has indicated

the presence of some one or more of the *heavy* metals, in which case a porcelain crucible must be used. The fused mass, when cold, is boiled for some time with distilled water, thrown on a filter, and the insoluble portion thoroughly washed.

I. Treatment of the portion insoluble in boiling water.

It may contain the *bases* mentioned above, some as *oxides*, and some as *carbonates;* and *silicic acid.* It is redissolved in hydrochloric acid (unless the preliminary examination has indicated the presence of lead or silver, in which case *nitric* acid must be used). The acid solution is examined systematically, according to the instructions already given.

II. Treatment of the portion soluble in boiling water.

It may contain certain *inorganic* acids, possibly also some *oxide of* TIN, *oxide of* ANTIMONY, *oxide of* IRON, and LIME.

The solution is divided into two parts (α, β).

α. *Tin*, *antimony*, *iron*, and *alumina* are specially tested for.

β. The inorganic acids are tested for.

II.—Preliminary Examination for Acids.

143. In the general preliminary examination of the compound under analysis, the following acids will (if the experiments have been carefully conducted) probably have been detected, viz. *hydrosulphuric acid*, *sulphurous acid*, *carbonic acid*, *chromic acid*, *arsenious* and *arsenic acids*, *silicic acid;* the acids of *chlorine*, *bromine*, *iodine*, and *fluorine;* the acids of *cyanogen* and of *nitrogen; oxalic*, *acetic*, and some other of the *organic acids*. Nevertheless, when several of these acids exist together, it is quite possible that some may be missed even by the most experienced analyst. A careful special testing should always, therefore, be had recourse to, and the operator must consider, by reference to the nature of the bases already discovered, what acid can *possibly* be in combination with them.

I. Treat a portion of the substance in a test-tube with concentrated sulphuric acid. Should a *greenish-yellow* gas, having the odour of chlorine, be evolved, it indicates the presence of one of the oxygen compounds of chlorine. This gas is highly explosive, and therefore the application of heat must be avoided; in the absence of this gas, apply heat.

A. It becomes *black*, evolving gases (amongst which *sul-*

phurous acid can be recognized), and a strong odour of burnt sugar. *Tartaric* and *malic acids* must be specially sought for.

B. It is decomposed *without* changing colour, evolving gas, but no odour of burnt sugar.

a. The gas burns with a *blue* flame (carbonic oxide) and renders *lime-water* turbid (carbonic acid). The presence of *oxalic acid* is indicated.

β. The gas burns with a *blue* flame, and restores the blue colour of reddened litmus-paper (ammonia). The acids of *cyanogen* must be specially tested for.

γ. A gas or vapour is evolved which is not inflammable, and the substance is not blackened. *Carbonic*, *sulphurous*, *hydrosulphuric*, *hydrochloric*, *hydrofluoric*, *nitric*, *acetic*, *benzoic*, and *succinic* acids may be present.

δ. A volatile vapour is evolved having an agreeable odour, and burning with a clear white flame (acetone). *Acetic acid* is clearly indicated.

ε. A vapour is evolved which corrodes glass. *Hydrofluoric acid* is present.

II. Heat a portion of the substance with sulphuric acid and binoxide of manganese.

a. *Chlorine* is evolved.

β. *Violet* vapours are evolved which colour starch-paste *blue*. *Iodine* is indicated.

γ. Dense *red* vapours are evolved which colour starch-paste *orange*. *Bromine* is indicated.

III. Heat a portion of the substance with sulphuric acid and copper filings, *brown-red* fumes are evolved. One or more of the *acids of nitrogen* are present.

IV. Heat a portion of the substance with dilute hydrochloric acid.

a. A colourless gas is evolved which renders lime water milky. *Carbonic acid* is present.

β. A colourless gas is evolved which blackens lead-paper, and which possesses the odour of rotten eggs. *Hydrosulphuric acid* is present.

γ. A colourless gas is evolved, possessing the smell of burning sulphur. *Sulphurous acid* is present.

δ. *Red* vapours are evolved. *Nitric acid* is present.

General Rules for the Preparation of the Solution to be tested for Acids.

144. Since many *bases* would be precipitated by the reagents employed to detect the presence of acids in the wet way, *as a general rule*, every metallic oxide, but those included in Group I. (the alkalies) is removed from a solution before proceeding to test it for acids. This may nearly always be effected by boiling with carbonate of soda (1) in slight excess. In some cases, it may be necessary to remove the oxides of the heavier metals by hydrosulphuric acid and sulphide of ammonium.

(2) *Chromic acid*, if present, should be reduced by hydrosulphuric acid, and the oxide separated by ammonia.

(3) *Silicic acid* should be separated by evaporating to dryness, with excess of hydrochloric acid, redissolving the residue in dilute hydrochloric acid, and neutralizing by ammonia.

NOTE.—In this case the volatile acids—viz. hydrocyanic, hydrobromic, hydriodic, acetic, formic, succinic, and benzoic acids—cannot be found in the solution. Acetic acid may be tested for specially with sulphuric acid and alcohol. The presence of silicic acid does not interfere with the testing for succinic and benzoic acids by sesquichloride of iron, nor with that of hydrocyanic acid, hydrobromic acid and hydriodic acid by nitrate of silver.

(4) If the substance be insoluble in water, but soluble in acids, and if it has been found by the preliminary examination to contain an organic acid, or hydrocyanic, hydrobromic, or hydriodic acid, it should be boiled with carbonate of soda; the base remains in the residue either free, or combined with carbonic acid, and the acid is dissolved in combination with soda. The solution should be exactly neutralized by nitric acid previous to testing for acids.

(5) If the solution to be tested for acids contain ammoniacal salts, boracic, tartaric, and citric acids cannot be recognized by the usual reagents. In such a case, the boracic acid may be tested for specially; or the ammoniacal salts may be removed by long-continued boiling with potassa, and the solution afterwards neutralized by nitric acid.

(6) If the substance be insoluble in water, but soluble in acids, and not a compound of an organic acid, or of hydrocyanic, hydrobromic, or hydriodic acids, a part may be dissolved in hydrochloric acid, and tested for all acids but hydrochloric,

and another part in nitric acid, and tested for hydrochloric acid by nitrate of silver.

(7) *Carbonic*, *hydrosulphuric*, and *sulphurous* acids should be separated, if present, by a strong acid, and the solution neutralized, one part with *potassa*, in order to test for boracic, tartaric, and citric acids, the other part with *ammonia*, to test for the other acids. *Carbonic acid* may be recognized by the precipitate caused by transmitting the gas through baryta water. *Hydrosulphuric* acid is recognized by its odour and by its reaction with a salt of lead, and sulphurous acid is also recognized by its odour, and by the white precipitate occasioned by passing the gas through a solution of sulphuretted hydrogen.

The solution filtered from the precipitate occasioned by carbonate of soda, (1) is divided into four parts. One part (A) is rendered slightly acid by *hydrochloric acid;* another part (B) is acidified by *nitric acid;* a third part (C) by *acetic acid;* and the fourth part (D), after having been acidified by nitric acid added in slight excess, is again made slightly alkaline by the addition of a few drops of *caustic potassa.*

I. Examination of the Solution acidified by Hydrochloric Acid (A).

Chloride of barium produces a *white* precipitate insoluble by boiling with great excess of acid. SULPHURIC ACID is present.

NOTE.—It being possible that the carbonate of soda used in preparing the solution may contain *sulphate of soda*, a small portion of the hydrochloric solution of the substance prepared for the examination for *bases*, may advantageously be employed for the detection of sulphuric acid.

Sesquichloride of iron produces a *deep-blue* precipitate, and protosulphate of iron a *pale-blue* precipitate. HYDROFERROCYANIC ACID is indicated.

Protosulphate of iron produces a *deep-blue* precipitate; sesquichloride of iron no precipitate, but a brown coloration. HYDROFERRIDCYANIC ACID is indicated.

NOTE.—If a *dark-blue* precipitate has been produced *protosulphate of iron*, and a *dark-blue* precipitate also by *sesquichloride of iron*, it is probable that *hydroferrocyanic* and *hydroferridcyanic* acids are both present. Proof of the presence of the latter acid is obtained by the solubility of the red-brown precipitate, which it forms with nitrate of silver in *ammonia;*

the corresponding salt of hydroferrocyanic acid being insoluble in ammonia.

Sesquichloride of iron produces a *blood-red* colour, which is destroyed by solution of *chloride of mercury.* SULPHOCYANIC ACID is indicated.

NOTE.—It must be borne in mind that a similar coloration is produced with *acetic acid;* in this case however the colour is destroyed by *hydrochloric acid.* It must be remembered, moreover, that when solution of sesquichloride of iron *alone* is heated, its colour becomes considerably heightened.

II. Examination of the Solution acidified by Nitric Acid (B).

Nitrate of silver produces a *white* precipitate, insoluble even by boiling in strong *nitric acid,* but very soluble in *ammonia.* HYDROCHLORIC ACID is present.

NOTE.—*Hydrochloric acid* is, however, best sought for in a *nitric acid* solution of a portion of the original substance, as it is almost impossible to obtain carbonate of soda quite free from *chloride of sodium.*

Nitrate of silver produces a *yellowish-white* precipitate, soluble in ammonia, but not so readily so as chloride of silver. HYDROBROMIC ACID is indicated.

Confirmation.—Add *chlorine water* to a portion of the original solution, and then agitate with *ether,* which will take up the bromine, and acquire a more or less deep *yellow* tinge.

Nitrate of silver produces a *yellowish* precipitate, soluble with great difficulty in *ammonia.* HYDRIODIC ACID is indicated.

Confirm by the *blue* colour imparted to *starch paste.*

Nitrate of silver produces a *white curdy* precipitate, soluble in *ammonia* and in alkaline *cyanides.*

Confirm by the *peach-coloured* flame, produced when the gas evolved by heating the dried precipitate in a tube is ignited. HYDROCYANIC ACID is indicated.

NOTE.—As *chloride of silver* and *cyanide of silver* are both readily soluble in ammonia, a further test is required to distinguish *hydrochloric* acid in the presence of *hydrocyanic* acid. The precipitate produced by nitrate of silver leaves after ignition, in the case of pure cyanide of silver, only *metallic silver,* which may be dissolved by nitric acid; any residue remaining is chloride of silver, which is insoluble in nitric acid.

III. Examination of the Solution acidified by Acetic Acid (C).

Sesquichloride of iron produces a *yellowish-white* precipitate. PHOSPHORIC ACID is present.

Confirm by *molybdate of ammonia.*

Sulphate of lime produces a *white* precipitate, which, after ignition, is soluble with effervescence in hydrochloric acid. OXALIC ACID is present.

Chloride of calcium produces a *white gelatinous* precipitate. HYDROFLUORIC ACID is probably present.

Confirm by action on glass.

IV. Examination of the Solution rendered nearly neutral by Caustic Potassa (D).

Chloride of calcium produces a precipitate, soluble in *chloride of ammonium*, and in *caustic potassa* in the cold. TARTARIC ACID is present.

Chloride of calcium produces no precipitate till ammonia or lime water is added and the whole boiled. CITRIC ACID is present.

NOTE.—The recognition of *tartaric* and *citric* acids, when both exist together in a solution, requires considerable care. If a precipitate has been produced by *chloride of calcium*, it must be filtered off; and the filtrate tested for citric acid by adding ammonia and boiling. When *tartrate of silver*, formed by precipitating a solution containing tartaric acid with nitrate of silver, is gently heated with ammonia in a test-tube, a shining mirror of metallic silver is deposited; a similar mirror is formed with citric acid, but only after long boiling.

Sesquichloride of iron produces a *yellowish-brown* precipitate. BENZOIC ACID is probably present.

NOTE.—Indications of this acid will have been obtained in the preliminary examination.

Sesquichloride of iron produces a *reddish-brown* precipitate. SUCCINIC ACID is probably present.

NOTE.—If the solution contain at the same time *benzoic* and *succinic* acids, the latter may be recognized thus:—Digest the precipitate produced by sesquichloride of iron with ammonia; filter off any benzoate of iron which may be formed, add to the filtrate *chloride of barium*, *alcohol*, and *ammonia*, by which *succinic acid* is precipitated, succinate of the alkaline earths being insoluble in alcohol.

Sesquichloride of iron produces a *bluish-black* precipitate. GALLIC OR TANNIC ACIDS are indicated.

NOTE.—*Tannic acid* produces, with solution of gelatine, an insoluble curdy precipitate; gallic acid is not precipitated by *gelatine*.

BORACIC ACID is recognized by its action on turmeric paper, which it reddens, like an alkali. If a solution, containing a borate, be treated with slight excess of hydrochloric acid, and a piece of turmeric paper be immersed in the liquid and then dried at 212°, it will be found to have acquired a brownish-red colour.

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